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ADVERTISING RATES GIVEN ON APPLICATION.

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### REFRACTORY MATERIALS FOR FURNACE LINING.

In this issue we publish another article of Mr. F. A. J. FitzGerald's serial on electric furnace construction and operation. This article deals with one of the most important practical problems, not only of electrometallurgy, but of metallurgy; namely, to find a satisfactory refractory material for furnace lining. This must be adapted to the special requirements of each case, according to the method of operation of the furnace and the maximum temperature in the same. In every case the refractory material must stand the highest temperature attained in the furnace. Since there is a very wide range of temperature for the different furnace reactions, different refractory materials will be used for different reactions. Another requirement to be fulfilled in every case is that the material is a relatively poor heat conductor so as to reduce to a minimum the losses of heat by conduction and radiation. These requirements must be fulfilled equally well in ordinary metallurgical furnaces as in electric furnaces; the main difference between the two types, with respect to the above requirements, is that the electric furnace is used for reactions which require temperatures beyond the highest attainable in ordinary furnaces. Refractory materials for electric furnaces must therefore be able to stand much higher temperatures than those in ordinary furnaces; they must withstand the reducing action of the carbon in the charge at these high temperatures. For this reason those commercial refractory materials which have proven perfectly suitable in ordinary metallurgical furnaces can no longer be used in electric furnaces requiring the highest temperatures.

There are, however, other differences. As Mr. FitzGerald points out, the conditions are simplified in the electric furnace in so far as there are no troubles experienced in the use of fuel, combined with a powerful blast. On the other hand, the essential nature of the electric furnace introduces a new complication. This is due to the requirement that the refractory material should be as far as possible a non-conductor of electricity. Now, we know, some refractory materials which do not conduct the current at ordinary temperature, become conductors of electricity at very high temperatures; the filament of the Nernst lamp is an example. The problem is, therefore, pretty complicated, and all our readers will certainly appreciate the information given by Mr. FitzGerald on a subject about which very little has been published up to the present. Mr. FitzGerald shows that we have three different materials suitable for refractory materials in electric furnaces. For the lower ranges of temperature we have the series of silico-carbides, for the next higher range carborundum, for the highest temperatures charcoal. Mr. FitzGerald gives a great amount of useful information concerning

methods of employing these materials for furnace linings. He emphasizes the great importance of good heat and electric insulation. Of course, in numerous cases it will be possible to avoid any furnace lining, but methods for this purpose will be dealt with in an article in a coming issue.

#### THE FILM ON THE ALUMINIUM ANODE.

The extremely high affinity of aluminium for oxygen—indicated by its correspondingly high oxidation heat, and by the very high velocity of the reaction—is the chief reason of the difficulty of the reduction of aluminium. When the purely chemical process had spoken its last word on the manufacture of aluminium, it was necessary to resort to the electric current as the only agent capable of breaking up easily those fixed and difficultly-transformable compounds of strong metals, which are of such large occurrence in nature. The high affinity of aluminium for oxygen also seems one of the chief factors which render the electrolytic precipitation of aluminium from an aqueous solution so very difficult, since any aluminium which may be deposited tends immediately to reoxidize; Dr. Patten's recent, and to some degree successful, attempt to use a solvent containing no oxygen appears to confirm this view. The high affinity of aluminium for oxygen also appears to be responsible for that thin, invisible, yet always present film on an aluminium surface, which, under certain conditions, effectively prevents contact of the aluminium metal with the air, solution or other surrounding medium, wherever no special means are taken to break down the film. The difficulties in soldering aluminium are assumed to be chiefly due to this film. Again the film is active on an aluminium electrode by preventing the electric current to pass in one direction, but allowing it to pass in the other direction—the latter being that in which the current is able to reduce the film. This last property has been utilized in the employment of aluminium electrodes in electrolytic rectifiers and electrolytic condensers.

The nature and the properties of the film on the aluminium anode have been the subject of an extended experimental investigation of Mr. William Roy Mott, who has contributed a series of articles on it to our columns. In an article in our April issue Mr. Mott dealt with the corrosion of aluminium and its prevention; in our July issue with the dimensions of the films on aluminium anodes; in our September issue on the electric properties of the film, its specific resistance, dielectric strength, its specific inductive capacity, and the critical voltage. To our present issue he contributes a highly interesting article on colloidal precipitation upon aluminium anodes. He considers the composition and chemical nature of the film in the light of the general phenomena of colloidal precipitation. Solutions of chromates, phosphates, tartrates, citrates, etc., strongly precipitate colloidal aluminium hydroxide. The same electrolytes produce insulating films upon aluminium anodes. Analyses show that the insulating film consists of aluminium hydrates combined with basic salts of aluminium, or, stating it in another way, the film consists of aluminium oxide, water and acid radical. Aluminium hydroxide is first

produced on the aluminium anode, and this reacts with the electrolyte. The loose, incoherent aluminium hydroxide adsorbs the acid radical by its great chemical affinity to form a very hard, dense, insoluble solid which possesses great insulating power—the well-known properties of the film. The necessary thickness of the insulating film varies with different electrolytes. The valence of the acid radical is of decisive importance. Electrolytes containing acid radicals of high valence give high critical voltages and films of great specific resistance and high dielectric strength, and so thinner films are obtained—thus, less coulombs are required for the formation of the film. Mr. Mott's paper appears to give for the first time an explanation of the complex phenomena in the anode film, and since this explanation is also able to predict what to expect from new electrolytes, with respect to the properties of the film, formed on the aluminium anode, Mr. Mott's paper deserves the greatest interest of all interested in this subject which is of equal importance scientifically and practically.

#### ON THE REALITY OF ATOMS AND IONS.

In an interesting paper presented at the recent International Congress of Arts and Science in St. Louis, on present problems of organic chemistry, Dr. William A. Noyes raised his voice against the strong present tendency on the part of some chemists to claim that chemical science in the true sense includes only such portions of our knowledge as can be stated in accurate mathematical terms. Dr. Noyes considers it impossible to conceive that those theories with regard to structure which have guided the work of thousands of chemists for the last fifty years do not in some measure express the actual truth with regard to atoms and their relation to each other in organic compounds. Dr. Noyes emphasizes as his very firm conviction that we should not be content with rounding out organic chemistry as a descriptive science, nor even with adding to the number of empirical rules which enable us to predict certain classes of phenomena—but that we must, instead, place before ourselves the much higher ideal of gaining a clear insight into the nature of atoms and molecules and of the forces or motions which are the real reasons for the phenomena which we study. Evidently, Dr. Noyes does not consider the conception of the atoms and molecules to belong to those "empirical rules which enable us to predict certain classes of phenomena;" in his opinion, atoms are realities.

Dr. Noyes' note of warning against the exaggerated mathematical tendency in theoretical chemistry is, without doubt, timely, but it is doubtful whether he does not go to the other extreme by proclaiming atoms as realities. Maxwell has once stated the situation of theoretical physics most lucidly as follows: The first object is to simplify and reduce the results of previous investigation to a form in which the mind can grasp them. The results of this simplification may take the form of a purely mathematical formula or of a physical hypothesis. In the first case, says Maxwell, "we entirely lose sight of the phenomena to be explained; and though we may trace out the consequences of given laws, we can never obtain more extended views of the connection of the subject." This

is in fact the danger which confronts those chemists who rigidly follow the mathematical course attacked by Dr. Noyes. On the other hand, to quote again Maxwell, "If we adopt a physical hypothesis we see the phenomena only through a medium, and are liable to that blindness to facts and rashness in assumption which a partial explanation encourages." If these words had not been written in 1855, one might think they refer to some phases of the development of the electrolytic dissociation theory; and it would seem, the danger is the same if we conceive atoms to be realities. What Maxwell advocates in theoretical physics is the development of physical analogies, of mechanical models. An analogy or a model will never be supposed to be the thing itself, but only to represent or illustrate it in those respects for the illustration of which it was devised. There is, then, no danger of making unwarranted generalizations. On the other hand, in the vividness of its conceptions and fertility of its methods, a model is all that can be desired for the purposes of theoretical physics and chemistry; what is needed is a working hypothesis. The conceptions of atoms and ions have proved to be an enormously useful working hypothesis and this fact represents their merit in physical science. Whether atoms or ions really exist, is rather a question of metaphysics.

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As long as we bear in mind that a physical or chemical hypothesis or conception represents only a model, we develop the model only to such an extent as is necessary to illustrate those facts which we wish to illustrate. We are not liable to add any imaginary properties to our model beyond those which we need; but this danger at once arises when we forget that a physical conception is only a model, and when we consider it as a reality. Thus, the conception of atoms led the chemists to consider and define them as the smallest possible chemical masses, although there is nothing in the facts of the combining of elements in constant multiple proportions, etc., which would necessitate such a view. Of course, if we accept this definition of the atom, it is true that the development of the electronic theory has brought about an "explosion" not only of the atom, but of the atomic theory. In reality, however, there is nothing contradictory between those properties of the atom which we must attribute to it in order to illustrate the old well-known chemical facts of the combination of elements, and the more recent achievements of the electronic theory. As a matter of fact, the latter may be considered to satisfactorily supplement the old model of the atom in various points in which it was vague. For instance, with respect to valency, the model of a cuprous atom differs from that of the cupric atom, in that the latter contains one more positive electron. Moreover, as J. J. Thomson has shown, we can conceive the atom as a structure of electrons in such a way that we get a complete illustration of the periodic system of elements. The beauty and importance of these models is not diminished in the slightest degree if we keep in mind that we have to do with models only which may or may not represent realities.

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The electrolytic dissociation theory has undoubtedly been enormously successful for those purposes for the illustration

of which it was originally devised; namely, for the description of the phenomena in dilute aqueous solutions. In this field it has proven to be such a highly valuable working hypothesis that people who confessed to be doubtful as to the reality of atoms, acted as though they were sure of the reality of ions. The properties which had been contributed to ions for the illustration of the facts in dilute aqueous solutions, were at once assumed to explain also the phenomena in more concentrated solutions and in other than aqueous solutions. The fact that there is manifestly a connection between chemical affinity and degree of electrical ionization in aqueous solutions, was generalized into the statement that all instantaneous chemical reactions in any solution take place between ions. Prof. Kahlenberg has shown that a practically instantaneous reaction takes place between hydrochloric acid and copper oleate in a solution in dry benzene, although the solution does not conduct the electric current, and there is no evidence of the dissociation of either the copper oleate or of the hydrochloric acid. He concludes that the above generalization is wrong. Dr. Noyes tries to escape this conclusion by supposing that a substance not already in the form of ions may separate into them under the influence of a second substance with which it can react. This may or may not be so, but it is not clear how such an assumption can have any value as a working hypothesis. It is not a model made to describe facts, but an assumption made to reconcile artificially a generalization which is so far not proven with an established fact which appears to contradict it directly. Prof. Bancroft recently remarked that when one remembers that Goldschmidt has shown the undissociated substances to be the active masses in certain reactions, one wonders why there should be this frantic desire to make all reactions ion reactions; it has not proven itself a useful working hypothesis and therefore, by definition, it is valueless for the present.

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We think it was Helmholtz who first proposed the view that chemical affinity is electrical attraction between charged atoms. This scheme has become much more lucid by the development of the electronic theory and by the explanation of valency on the basis of this theory. Of course, if this general theory holds good, all chemical reactions are ionic reactions. This is undoubtedly a beautiful conception; if proven, it would make the whole field of chemistry a single chapter of the electronic theory. If we follow the present general course to explain everything by electrons, we will find it to be either right or wrong, and we will at least arrive at the limitations of the electronic theory. At present we must not forget that the electronic explanation of chemical affinity is so far only an unproven hypothesis. The case is quite similar to that of the mechanical theory of heat which has been predominant for such a long time in the explanation of heat phenomena. In fact, this hypothesis appears to have been so generally accepted that in his first paper on the principle of the conservation of energy, Helmholtz based his first proof on the mechanical theory of heat. In recent years, however, this theory has lost much of its glory, and this example should caution us not to rely too much upon very general hypothetical assumptions which are not directly based on experimental evidence.



### CHEMISTRY AT THE INTERNATIONAL CONGRESS OF ARTS AND SCIENCE.

The International Congress of Arts and Science held at the Universal Exposition at St. Louis, from September 19 to 25, was arranged with a view of bringing the scattered sciences and arts into closer mutual relations. This was to be accomplished by papers read by leading representatives of theoretical and applied sciences, in which the general principles and fundamental conceptions which connect groups of sciences should be set forth. The history of special sciences should be reviewed, their mutual relations should be shown and their present problems discussed. In the following a concise abstract of the proceedings of Department 10 (chemistry) shall be given. A report of Section E (technical chemistry) of Department 18 (technology) will be given in our next issue.

In the general meeting of Department (chemistry) the chairman, Prof. J. M. Crafts, pointed out that mathematics is now doing for chemistry what Newton once did for astronomy. Prof. J. U. Nef reported on the decomposition points in alcohol and ether, while Prof. F. W. Clarke spoke on the importance of physical chemistry.

In Section A, devoted to inorganic chemistry (Chairman Prof. J. W. Mallett), Sir William Ramsay delivered an address on molecular weights. He pointed out that all chemical discoveries show an intimate connection with the methods of research. A splendid classification of the elements was given by Lothar Meyer and Mendelejeff in their system of elements. The recent discoveries of radium, polonium, etc., are especially interesting to physicists, while the gases originating from the emanation of radium lead to the new elements of the argon group. It has been found that the chemical compounds of nitrogen show a molecular weight of nitrogen different from that of nitrogen alone. It has also been found that Avogadro's law is not exact. Thus new views are opened for research in the field of molecular weights.

Prof. H. Moissan spoke on "Mineral Chemistry in Relation to the Other Sciences." He gave an outline of the different periods of chemistry. First the view was held that the chemical elements are to be found in water, fire, air and earth. After the views on elements had been cleared up, the laws of chemistry were investigated by men like Gay Lussac, Richter and others. After the period of establishing laws there followed a period of experimental work. Stas determined the molecular weights. Finally mineral chemistry having been developed, organic chemistry was founded. The latter was predominant during the last half of the nineteenth century until at its end new paths were opened for inorganic chemistry. Discoveries like that of Gauthier that arsenic is present in all animal and vegetable organisms show that mineral chemistry plays an important role also in organic life. The speaker concluded with the remark that Faraday's words still hold good to-day that chemistry is an experimental science.

In Section B, devoted to organic chemistry (Chairman Prof. A. B. Prescott) Prof. W. A. Noyes spoke on the present problems of organic chemistry. The successive steps which have lead to our present standpoint in organic chemistry are the discovery of isomerism, the discovery of radicals, the old radical theory, the theory of types, the establishment of true molecular weights, the discovery of the fact of valence and the determination of structure. The object of future researches must not only be to round out organic chemistry as a descriptive science or to add to the number of empirical rules which enable one to predict certain classes of phenomena, but rather to gain a clear insight into the nature of atoms and molecules and of the forces and motions which are the real reason for the chemical phenomena. The author gave a general outline of the applications of the electronic theory to the atomic theory. Prof. J. Stieglitz discussed the formulae of the speed of certain organic reactions.

In Section C, devoted to physical chemistry (Chairman Prof. Wilder D. Bancroft), Prof. J. H. van't Hoff gave an histori-

cal outline of the researches on the nature of mass and on the nature of affinity. His sketch was based on a table containing the names of the investigators in the field of theoretical chemistry. His own name was not mentioned by the speaker, but this omission was made good by Prof. W. Ostwald, who pointed out that the two fields of chemical research which have to do with chemical masses and chemical affinity respectively, were joined by the work of van't Hoff. At the same time Ostwald attacked the atomic theory by pointing out that as a result of the recent researches on radium and of the development of the electronic theory, the atom has "exploded."

In Section D, devoted to physiological chemistry (Chairman Prof. W. O. Atwater), Prof. Sohnheim discussed the food problem, which is on the boundary line of physiology and national economy. Physiology has shown that albumen, fat and hydrocarbons can replace each other for purposes of food, exactly according to their calorimetric values. The only exception is that the daily food of man must contain about 100 grams of albumen. The thermal equivalent of the total amount of daily food varies between 2200 gram calories and 4500 gram calories, according to the work done by the muscles. A man who does not do hard, laborious work must, therefore, consume relatively a greater quantity of albumen in proportion to his total food than a man doing hard, laborious work. This fact is well known and has led to an exaggerated opinion of the importance of albumen in food. If the proportion of albumen in food is too large, the content of cellulose is relatively small and the digestion is not normal. This is the reason why people who do brain work need sports like golf.

Prof. R. H. Chittenden spoke on the present problems of physiological chemistry and especially on those points which lack explanation.

### ANDREW CARNEGIE AS BESSEMER MEDALIST.

The annual meeting of the (British) Iron and Steel Institute was held in New York City from October 24 to October 27. It was the second meeting held in this country, the other one having been held fourteen years ago. The first session, on October 24, at Sherry's, was memorable by the presentation to Mr. Andrew Carnegie of the Bessemer gold medal, the presentation speech being made by Sir James Kitson. Sir James dwelt at length upon Mr. Carnegie's achievements in the iron and steel industry, and spoke of a visit he made to the Pittsburg steel works many years ago with Mr. Carnegie as his guide, when, in response to a question, Mr. Carnegie confessed that he did not understand the intricate machinery employed in his works, but said he did believe he understood the man who was behind the machinery and running it. Taking this as his text, Sir James spoke of Mr. Carnegie's general attitude toward inventors and others who had been of such vital importance in building up the iron and steel industry.

Mr. Carnegie, accepting the medal, replied somewhat briefly, but with evident feeling, saying among other things that there were several kinds of men—the man who did great things and did not get credit for it, the man who did great things and did get credit for it and the man who got credit for about ten times more than he ever did, and to this last category Mr. Carnegie modestly consigned himself. He did give himself credit, however, for the possession of common sense and quoted the epitaph which several times he has said he wanted placed on his tomb: "Here lies one who knew how to get around him, men cleverer than himself." Mr. Carnegie concluded with the remark that he hoped to hold his medal and pass it on to his descendants as he received it—pure gold and untarnished.

Prior to the presentation of the medal Mr. Fornes, as the representative of the Mayor of New York City, made a speech of formal welcome on behalf of the city, to which Mr. Carnegie, as president of the Institute, replied.



# REFRACTORY MATERIALS IN ELECTRICAL RESISTANCE FURNACES.

By F. A. J. FITZGERALD.

In those cases where electrical resistance furnaces are used for relatively low temperature work the problem of finding a satisfactory refractory material is not always more serious than in the case of ordinary furnaces. In some ways the problem is simplified because the troubles experienced in the use of fuel, combined with a powerful blast, are absent. On the other hand, in the electric furnace new problems are encountered; such, for example, as the increased electrical conductivity of the refractory materials when raised to a high temperature, the reducing action of carbon on the compounds of which the refractory material is composed, etc.

When the electric furnace is used for work requiring a very high temperature the problem of obtaining a satisfactory refractory material becomes serious. None of the ordinary refractory materials is satisfactory, and it may be said that no thoroughly suitable refractory material exists. As an illustration of the troubles experienced in the ordinary refractory materials, an experiment in which some Buttersen muffles were used may be described. The muffles were heated by covering their tops and bottoms with a resistance material composed of granular coke, through which a current was passed. Satisfactory results were obtained so long as the temperature of the resistance material was not pushed very high, but when the attempt was made to get a high



FIG. 1.—HOLES FUSED IN MUFFLES BY TOO HIGH A TEMPERATURE.

temperature in the granular coke the muffles were fused as shown in Fig. 1. Examination of the photograph will show that the holes fused in the muffles are surrounded by a mass of granular coke, agglomerated by the fused fire clay. Not only has fusion taken place, but it is found that the material of which the muffles are made has been reduced by the carbon, for many grains of the latter are covered with a light green

colored substance that is readily recognized as amorphous silicon carbide. In places, too, there are found metallic particles of a silvery lustre, these being composed of an alloy of silicon and aluminium, produced by the reduction of the constituents of the muffle. It would have been possible to attain the desired object in this experiment without fusing the muffles; but one of the greatest advantages in the use of the electric furnace is the possibility of having the *source of heat* at a very much higher temperature than that required for the work in hand. When heat is conveyed from a source at a temperature  $T$  to a substance at a temperature  $\theta$ , the rate at which the temperature of the latter is raised is a function of  $T-\theta$ , and the greater the value of  $T-\theta$  the more rapidly will the temperature of the substance be raised. As  $\theta$  increases the value of  $T-\theta$  decreases, consequently, the amount of heat conveyed per second from the source to the substance becomes less. Where the source of heat is at a temperature but little higher than that to which it is desired to raise the substance, the attainment of the final temperature takes a long time. Herein lies the economy of an electrical source of heat for many purposes, for it is possible to have the source of heat at a much higher temperature than that required in the substance, so that the transference of heat is very rapid. In the case of the experiments with the muffles, the desired temperature was below that of the fusion of the materials of which the muffle was composed, but it was so close to it that there would have been no advantage in using an electrical source of heat.

In many purposes for which the electrical furnace is used, the ordinary refractory materials, such as silica, magnesite, dolomite, etc., may be used; but where the temperature is much above that used in ordinary furnaces it becomes necessary to look for some other substances. The most promising substances for this purpose are found in certain products of the electric furnace, and special reference will be made here to certain compounds of carbon and silicon which seem to be of considerable value as refractory materials.

The earliest literature bearing on refractory compounds containing silicon and carbon or silicon carbon and oxygen is found in certain papers read by Colson and Schutzenberger in 1881 before the Paris Académie des Sciences. In one of these they describe an experiment in which they heated silicon strongly in a porcelain tube, through which a current of carbon dioxide gas was passed, with the result that the silicon was changed into a green-colored mass which was subsequently purified from silicon and silica by heating in potassium hydrate solution and hydrofluoric acid, respectively. The residue was a green-colored powder which was unattached by acids or alkalis, and was found to correspond to the formula  $\text{SiCO}$ .<sup>1</sup>

In another experiment Colson made a mixture of silicon and lamp black which he raised to a white heat and thus obtained a compound having the composition  $\text{Si}_2\text{C}_3\text{O}$ .<sup>2</sup>

By heating silicon in a current of carbon bisulphide Colson obtained the compound  $\text{Si}_2\text{C}_3\text{S}$ . When this substance was heated in a current of oxygen  $\text{SO}_2$  was evolved without any change in weight of the sample, thus indicating the formation of a compound  $\text{Si}_2\text{C}_3\text{O}_2$  ( $\text{Si}_2\text{C}_3\text{O}$ ) which composition was confirmed by analysis.<sup>3</sup>

In 1892 Schutzenberger presented a paper in which he spoke of the various compounds as having "nearly the same appearance and not clearly distinguishable, except by analysis. They are powders of a more or less pale green color, infusible, stable, unattacked by hydrofluoric acid and caustic alkali solutions, even when concentrated: attacked at a dull red heat by fused potassium hydrate with liberation of hydrogen and formation of potassium silicate and carbonate \* \* \* \* In all of them the carbon, combined with silicon, resists combustion at a red heat in free oxygen, or by means of cupric oxide, in a remarkable manner. The carbon of these carbo-silic compounds is not completely burnt except by heating with lead chromate."<sup>4</sup>

Schutzenberger then goes on to describe how he obtained a new compound,  $\text{SiC}$ , by heating powdered silicon mixed with silica in a carbon crucible.

In 1893 Acheson, in a paper read before the Franklin Institute, describing the carborundum furnace, said:

"W represents a white or gray-greenish looking shell, surrounding the zone of carborundum crystals. The mass consists of small pieces of the size of the original sand grains. These pieces are soft and may be reduced very easily to a fine powder. The qualitative analysis showed that the powder had the same constituents as the carborundum crystals, and the powder was, therefore, cleaned in the same manner as in the case of those crystals. The white-green shell was crushed and alternately heated with hydrochloric acid, caustic soda, water, hot oxygen and hydrofluoric acid. The resulting powder had the following composition:

C	27.93
Si	65.42
$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$	5.09
CaO	0.33
MgO	0.21

"We may say, then, that the powder consists essentially of carbide of silicon. But this carbide of silicon is different from the other one, in that it forms no crystals, is amorphous

<sup>1</sup> Comptes Rendus, XCII., p. 1506.

<sup>2</sup> Comptes Rendus, XCIV., p. 1316.

<sup>3</sup> Comptes Rendus, XCIV., p. 1528.

<sup>4</sup> Comptes Rendus, CXIV., p. 1067.

and very soft, and of no value as an abrasive. It has been obtained at a comparatively low temperature—far distant from the core—and is identical with the product recently obtained by P. Schutzenberger."<sup>2</sup>

In 1896 F. Leuermann published the results of his investigations on the use of silicon carbide as a substitute for ferro-silicon, and asserted that the amorphous form of that compound was insoluble in molten steel.<sup>3</sup>

In 1899 a patent was granted to Benjamin Talbot for a "Lining for Metallurgical Furnaces." In the specification Talbot says he has found carbide of silicon to be very refractory under high temperatures, and that it resists the fluxing action of acid and basic slags. To use the carbide as a refractory material it is mixed with some suitable binding agent and moulded into forms, such as bricks, etc. He prefers to use the amorphous form of silicon carbide, since "that has hitherto been deemed a waste product and is consequently inexpensive."<sup>4</sup>

In 1900 Engels obtained a patent for fireproofing materials by coating them with carborundum, which was afterwards caused to unite with the material by fusing (!) the carborundum with an arc. Later he took out two more patents along similar lines.<sup>5</sup>

In 1903 two patents were issued to E. G. Acheson: One on a "Method of producing compounds containing silicon, oxygen and carbon;"<sup>6</sup> the other on a "Refractory material."<sup>7</sup> The refractory material is called "siloxicon," and contains silicon, carbon and oxygen. The siloxicon is produced by heating in an electric furnace a mixture of carbon and silica, the latter being in excess over the amount required for the formation of silicon carbide. An experiment is described in the specification, and the resulting substance gave the following analysis:

Silicon	57.7
Carbon	25.9
Iron	2.1
Aluminium	0.4
Calcium	trace
Magnesium	trace
Oxygen (by difference)	13.9
	100.0

Various compounds appear to be formed according to the methods of manufacture. Acheson says:

"Thus I have made in this way a compound corresponding approximately to the composition  $\text{Si}_2\text{C}_2\text{O}$ , which has been described by Colson as resulting from an oxidation of the compound  $\text{Si}_2\text{C}_2\text{S}$ , or from heating silicon in carbonic acid gas. (*Comptes Rendus*, 1882; 94, page 1526.) I have also made analogous compounds wherein the silicon and carbon are in atomic proportions, but wherein their ratio to the oxygen varies within considerable limits. For instance, I have produced a compound  $\text{Si}_2\text{C}_2\text{O}$ ."

Siloxicon is described as having a density of 2.73; a gray-green color when cold, and light yellow when heated to 300° Fahrenheit or over; the property of forming a coherent mass when ground, moistened with water, moulded into a form and fired; a very refractory nature; a neutral action with both acid and basic slags; as being insoluble in molten iron; indifferent to all acids except hydrofluoric acid which attacks it slowly; finally, it resists the action of hot alkaline solutions. Acheson has also shown that siloxicon is oxidized at high temperatures in an oxidizing atmosphere. Assuming the compound to have the composition  $\text{Si}_2\text{C}_2\text{O}$ , the oxidizing

action probably takes place according to the following equation:

$$\text{Si}_2\text{C}_2\text{O} + 7\text{O} = 2\text{SiO}_2 + 2\text{CO}_2$$

In *The Foundry* of August, 1904, F. J. Tone describes "Carborundum Firesand," a name applied to the amorphous substance found outside the zone of crystalline material in the carborundum furnace. It is said to be formed at a temperature "between 6000° and 7000° Fahrenheit." Chemically it is "a compound of carbon with incompletely reduced silica;" it always carries a certain proportion of free silica; it has a specific gravity of 2.7; it is grayish green in color, and has a low heat conductivity. It is said to be an excellent material for furnace linings.

This completes the review of the principal literature relating to the amorphous compounds of carbon and silicon, or carbon, silicon and oxygen. The subject has been treated at some length because it is believed that these substances, which for convenience may be called *silico-carbides*, will prove of value in the construction of electric furnaces. The silico-carbides obviously have their limitations, among which may be noted their conversion into carborundum at high temperatures. However, there is a considerable range of temperature between that at which ordinary refractory materials break down, and the temperature of formation of crystalline silicon carbide. For this range of temperature the silico-carbides will be of value. There has been very little published as to the use of the silico-carbides in electric furnaces, and in what follows some of the results of the experimental work of the writer, with the collaboration of Mr. P. McN. Bennie, are given.

As an example of the application of the silico-carbides to electric furnace construction, it will be found that in many cases a comparatively thin layer of the substance will effectually protect fire bricks from fusion. A very simple form of furnace, useful for some purposes, may be made by forming a trough of fire bricks, placing the terminals connected with the source of current at either end and then filling the trough with granular carbon which serves as the heating resistance. If the temperature of the granular resistance is raised to a bright white heat, the bricks will be fused and the working of the furnace will be unsatisfactory. This can be effectually prevented by lining the trough with a layer of a silico-carbide. Assume, for example, that it is desired to embed crucibles in the granular resistance for the purpose of melting a ferro-alloy. The trough is then built about two inches deeper and four inches wider than is needed for the proper cross-section of the heating resistance. A layer of the silico-carbide, two inches thick, is spread on the bottom of the trough; pieces of sheet iron are then set up two inches away from the side walls of the trough, and the spaces between the walls and the sheet iron filled with the silico-carbide. Finally, the space between the sheet iron pieces is filled with the granular carbon, and the crucibles put in place. Where the temperature is not excessively high this method gives very satisfactory results.

To substitute bricks made of a silico-carbide for fire brick, dispensing with the latter altogether, is not advisable, since the silico-carbides are much better heat conductors than ordinary fire bricks. Hence, if they are used alone they cause a serious loss of heat and should not be used, except in those places where a good heat-resisting material is required.

In F. J. Tone's article, already quoted, a low heat conductivity is spoken of as characteristic of "Carborundum Firesand." An experiment illustrative of this characteristic is described as having been performed by a certain manufacturer of tilting furnaces.

"With fire brick linings first employed it was possible to obtain from five to six heats per day. With the first trials of carborundum firesand nine to ten heats were easily run, and he expects to reach a still higher efficiency. The exterior of

<sup>2</sup> Journal of the Franklin Institute, September, 1893.

<sup>3</sup> Zeitschrift für Electrochemie (1896), III., p. 113.

<sup>4</sup> U. S. Patent 628,258, July 4, 1899.

<sup>5</sup> U. S. Patent 650,040, May 22, 1900; U. S. Patent 734,457, July 21, 1903; U. S. Patent 734,458, July 21, 1903.

<sup>6</sup> U. S. Patent 722,792, March 17, 1903.

<sup>7</sup> U. S. Patent 722,793, March 17, 1903.

<sup>11</sup> ELECTROCHEMICAL INDUSTRY, Vol. I, No. 11, p. 373.

the furnace is cool enough to rest one's hand on the shell, and the plain inference is that the refractory we are discussing is an exceptionally good insulator of heat."

Unfortunately, the kind of fire brick lining compared with the carborundum firesand is not mentioned. Nor is it explained whether the lining used in the experiment was composed of the carborundum firesand alone, or whether it was backed with fire brick. The insulating properties of the silico-carbides may be greatly improved by keeping them in a porous state; but according to the writer's observations the silico-carbides are not good heat insulators. This was well illustrated in the case of a small gas furnace, where siloxicon was substituted for the fire clay lining, with the result that although a steel melt could easily be obtained in the furnace under ordinary conditions, the heat was conducted away so rapidly by the siloxicon that it was almost impossible to melt copper.

It is well known that those substances which are excellent electrical insulators at ordinary temperatures become to a greater or less extent conductors when raised to a high temperature. The phenomenon is frequently observed in the working resistance furnaces and becomes marked where the heating resistance has a high resistivity. This is illustrated in furnaces of the Cowles type where a current is passed through a mixture of an oxide and carbon which has a high resistance, for if the lining of the furnace becomes very hot there will be distinct current leakage. In a resistance of granular graphitized coke, the leakage effect is far less marked, since the ratio of the electrical resistances of the lining and the heating resistance is always great.

Fortunately, the silico-carbides are fairly good insulators, though they probably are better conductors than ordinary fire brick, heated to the same temperature. We have made an experiment with the object of gaining some information on this point, the conditions being so adjusted as to obtain the maximum leakage effect.

A small box was built with the bottom, and two sides composed of silico-carbide tiles, 12 inches long, 6 inches wide and 2 inches thick. The tiles were made by mixing three parts of the silico-carbide with one part of tar and the mixture tamped into moulds which were then baked at a high temperature in a non-oxidizing atmosphere. The silico-carbide used contained about 5 per cent of free carbon in the form of graphite, and in addition to this there was the carbon deposited from the tar, so that the conditions were very favorable for considerable leakage of current. The ends of the box were formed of graphite blocks which were connected with a source of electric current. When finished, the inside dimensions of the box were: Length, 12 inches; width, 1½ inches; depth, 6 inches. The box was filled with granular graphitized coke, contact between the granular coke and the graphite blocks being made by graphite powder tightly rammed into place. The graphite powder also made good electrical contact between the blocks and the silico-carbide tiles.

The current was then thrown on, and when the tiles were raised to a good red heat, the ammeter reading was taken, also the voltage difference between the graphite blocks. One of the tiles forming the side of the box was then removed and the granular carbon quickly raked out. The moment this was done, and before appreciable cooling of the remaining tiles had taken place, the ammeter and voltmeter readings were again taken. The results obtained were as follows:

	Before removal of granular coke.	After removal of granular coke.
Ammeter .....	340 amps.	100 amps.
Voltmeter .....	15 volts	33 volts
Sectional area of granular coke .....	9 sq. ins.	0 sq. ins.
Sectional area of tiles (total) .	36 sq. ins.	24 sq. ins.

The explanation of the increased voltage after the removal of the granular coke is that there was a resistance in series with the box; consequently, when the coke was removed, there was a redistribution of the development of energy in the circuit.

Now let the electrical conductance of the box before removing the granular carbon be  $C$ , and after removal of the carbon be  $c$ , then,

$$C = \frac{340}{15} = 22.7.$$

$$c = \frac{100}{33} = 3.0$$

Since the sectional area of the tiles was 24 square inches when the granular carbon was removed, the value of the conductance for a sectional area of 36 square inches would be,

$$3.0 \times \frac{36}{24} = 4.5$$

and the conductance of the granular carbon would be,

$$22.7 - 4.5 = 18.2$$

Since the conductance varies directly as the sectional area of the conductor, we have for the ratio of the conductivities the following equation:

$$\frac{\text{Conductivity of granular carbon}}{\text{Conductivity of silico-carbide tile}} = \frac{18.2}{4.5} \times \frac{36}{9}$$

$$= \frac{72.8}{4.5}$$

From this result it may be deduced that in a furnace having a carbon resistance of the kind used in the experiment, with solid walls of silico-carbide, of which the total sectional area was the same as that of the carbon resistance, and with all other conditions the same as in the experiment, about 6 per cent of the current would be lost by leakage.

In actual practice, however, there would not be any such leakage for all the conditions of this experiment were such that the leakage was a maximum. The experiment, therefore, must be considered as an exaggerated case serving to illustrate the possibilities of leakage.

As to the best method of moulding silico-carbides into forms such as bricks or tiles, it depends to a certain extent on the use to which they are to be put. When the material is put directly into place in the furnace, where it will not have to undergo any serious mechanical strains, a mixture of the powdered silico-carbide, and a solution of glue in water gives satisfactory results. In order to obtain the best results with this method the mixture should be used hot. In those cases where very high temperatures are reached this method of making bricks is to be particularly recommended, for the silica which is usually present in commercial silico-carbides is fused at high temperatures, and thus strengthens the article considerably.

When there is no free silica present, and the article is made up with the glue solution, it becomes very weak and crumbles after use. It is, therefore, advisable to analyze the silico-carbide before using, and if there is no silica present a small quantity may be incorporated with the mixture. The best form of silica for this purpose is infusorial earth. The presence of silica is sometimes objectionable, as will be shown later.

In cases where the bricks will not be exposed to such high temperatures the silico-carbide may be mixed with a dilute solution of sodium silicate. The solution used for this purpose should not, as a rule, have a greater density than 1.03 to



1.05. Tone recommends a solution having a density of 33° Beaumé (1.277), but this is for ordinary furnaces, where relatively low temperatures are used. For high temperature work a solution of this density would introduce too much sodium silicate for satisfactory results.

A very satisfactory bond for silico-carbides is found in gas tar. A good mixture contains 4 parts of the silico-carbide to 1 part of tar. In using tar, however, it must be remembered that a residue of carbon is left in the article, and this tends to diminish the insulating properties of the silico-carbide. It should also be noted that if the article is exposed at high temperatures to an oxidizing atmosphere the carbon residue which acts as the binding agent is burnt out. If this happens the article will disintegrate, unless the temperature and oxidizing conditions are such as to cause oxidation of the silico-carbide and consequent binding together of the particles as discussed below. When, therefore, the article is exposed to oxidizing actions and a comparatively low temperature, it is better to use sodium silicate as the binding agent. But where the conditions are such that neither oxidation or serious current leakage is to be feared, the tar bond is very satisfactory, giving articles of considerable mechanical strength.

When an article of great mechanical strength is required, and the use of tar is objectionable, the best method of making the article is by causing the particles of the silico-carbide to frit together by oxidation. To accomplish this result the silico-carbide is mixed with some temporary binding agent, such as a solution of glue in water and then heated to a high temperature for several hours in a strongly oxidizing atmosphere. By this treatment the grains of the silico-carbide are superficially oxidized. In the case of amorphous silicon carbide this would take place according to the equation:



If the article made in this way is examined under a strong lens, it will be seen that the grains of carbide are superficially oxidized and fused together in that way. By this method articles of great mechanical strength can be made. It should be noted here that the formation of silico-carbide articles by the oxidation method requires prolonged heating, since the rate of oxidation is slow, proceeding gradually from the outside of the article to the center.

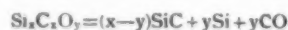
The use of silico-carbides is limited to certain temperatures, for, beyond a certain temperature, crystalline silicon-carbide (carborundum) is formed. Judging from the literature on the subject, the silico-carbides vary greatly in their composition, although, as Schutzenberger pointed out, their general properties seem to be similar. If a silico-carbide article, composed substantially of amorphous silicon-carbide, is heated to the temperature of formation of carborundum, the change produced is simply one of physical characteristics: The amorphous substance is converted to the crystalline state.

Another important change takes place if silica happens to be present, for the silicon is produced according to the equation:



The silicon thus produced may remain, for some time at least, distributed throughout the article; but if the temperature is high, it will be rapidly vaporized.

If the article is assumed to be substantially composed of a compound having the formula  $\text{Si}_x\text{C}_y\text{O}_z$ , then at high temperatures decomposition according to the following equation takes place:



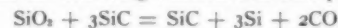
The reactions that take place when silica or a silico-carbide containing oxygen are present must be kept in mind, since the presence of silicon vapors in the furnace may be objectionable.

While considering the effect of the presence of silica in the refractory material it is well to note that silica has an appreciable vapor tension even at relatively low temperatures. This fact was recently noted by Moissan in connection with some experiments on the action of lime and carbon when heated to the temperature of fused platinum. In his experiments, Moissan placed a graphite boat containing a mixture of lime and sugar-carbon in a silica tube. The tube was placed in a small furnace built of blocks of lime and heated by an oxygen and illuminating-gas flame. Moissan says:

"Repeating and varying this experiment we observed a somewhat interesting fact; this is, that silica has an appreciable vapor tension at a temperature below that at which softening takes place. Accordingly, when heating the mixture of carbon and lime to about 1200° C. small needles of silicate of calcium, insoluble in water or dilute acids, are seen to form slowly on the surface of the lime. This appreciable vapor tension of silica below its temperature of fusion will, unfortunately, limit the number of experiments that may be performed at high temperatures in silica tubes."<sup>12</sup>

This vaporization of silica at relatively low temperatures seems to be confirmed by a common phenomenon in electric furnaces. Where carbon and silica are both present, although not necessarily in contact, specimens of the former are frequently found to be covered with a green-colored deposit which, on examination, is found to be the amorphous form of silicon-carbide. It follows, therefore, that in using the silico-carbides as refractory materials, it is necessary to keep in mind this appreciable vapor tension of silica, when for any reason it is undesirable to have silicon present as an impurity.

When the temperature to which the refractory material is submitted may be up to or above that of the formation of carborundum, it may be advisable to use crystalline silicon-carbide in the first place. It is possible, however, to use a silico-carbide at first, allowing it to be converted into carborundum *in situ*. If this is done the silico-carbide should first be analyzed to determine whether oxygen compounds are present or not. If oxygen compounds are present in appreciable quantities the silico-carbide may be unsuitable for the work. Assume, for example, that the silico-carbide is mainly composed of amorphous silicon-carbide, but that a certain amount of silicon is present: then at the temperature of formation of carborundum the following reaction will take place:



The result is that the refractory article or lining will be impregnated with metallic silicon, or the furnace will be filled with silicon vapor. When the presence of the silicon is unobjectionable this reaction may be disregarded; otherwise there are two courses open:

(1) The silica may be removed or a material free from silica obtained.

(2) From the analysis of the material the amount of carbon necessary to eliminate the oxygen and to form carborundum may be added to the mixture.

When it is desired to use carborundum directly as a refractory material the binding agents already suggested for silico-carbides may be used. Carborundum may also be made into a strong article by the oxidation method as described when dealing with the silico-carbides.

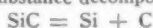
Another method of making articles of carborundum is by recrystallization. The carborundum in the form of grains or powders is mixed with some adhesive substance, such as a solution of glue in water, the mixture moulded in the desired form and the article then placed in an electric furnace and heated to the temperature of formation of carborundum. This causes a recrystallization of the carborundum and forms a strong article which preserves perfectly the form in which it was moulded.

<sup>12</sup> Comptes Rendus (1904), CXXXVIII., p. 244.

The current leakage effect at high temperatures seems to be somewhat more marked in carborundum articles than in the case of the silico-carbides.

Neither the silico-carbides nor carborundum can be used as refractory materials where they come in contact with fused alkalis, since these produce rapid decomposition. They are also attacked by chlorine at high temperatures. It is said that siloxicon and carborundum firesand are not attacked by molten metals or slags, whether acid or basic. While this may be true at relatively low temperatures, it most certainly is not true so far as high temperatures, such as those attained in the electric furnace, are concerned. If carborundum or the silico-carbides are in contact with fused fire brick, for example, at a high temperature, there is a marked reaction, with the formation of a silicon-aluminium alloy.

The temperature limit to the use of carborundum is reached when that substance decomposes according to the equation:



the silicon escaping as vapor, while the carbon remains as graphite. When the temperature is so high that this decomposition occurs, there appears to be no refractory material that can be used, except carbon. The best form of carbon for this purpose is charcoal, since its electrical resistivity is high. Where carbon cannot be employed then the furnace must be so constructed that the use of a refractory material at the place of high temperature can be dispensed with. That subject, however, belongs rather to furnace design than to a discussion of refractory materials.

It seems that where temperatures higher than those at which ordinary refractory materials can be employed are obtained, we are confined to the use of the silico-carbides, carborundum and carbon. All these have their disadvantages; but so far there does not appear to be any remedy. However, it is to be hoped that with further study of electric furnace products other refractory materials will be discovered that may be used where those discussed above are unsatisfactory.

No attempt has been made here to discuss the chemistry of the silico-carbides. The literature on the subject seems to show that there are several different compounds of variable composition, and it may be that their properties vary with the chemical composition. It was pointed out that it is sometimes necessary to analyze the silico-carbide, and in such cases the following methods have been found to give good results, fulfilling all technical requirements. The methods also apply to the analysis of carborundum.

#### ANALYSIS OF SILICO-CARBIDES AND CARBORUNDUM.

**Preparation of Sample.**—The sample must be reduced to a very fine powder. This is highly important, for, unless the powder is very fine, decomposition by the reagents employed will not be complete.

**Free Carbon.**—A weighed portion of the sample is heated in an open porcelain crucible, the contents being frequently stirred with a platinum wire. It will be found advantageous to support a long piece of combustion tube to bring vertically over the crucible, thus creating a draught of air over the contents of the crucible, causing the more rapid combustion of the carbon. When the carbon is completely burnt the crucible and its contents are weighed, the loss in weight giving the free carbon. The result obtained may be too low, even if the carbon is completely burnt, because of oxidation of the silico-carbide or carborundum, as the case may be. The error introduced in this way, however, is small, unless the crucible has been raised to a very high temperature.

**Free Silicon.**—A weighed portion is digested with a concentrated solution of sodium hydrate, the solution diluted, filtered off and the silica separated from the filtrate in the usual way. If the sodium hydrate solution contains sodium silicate an appropriate correction must be made. A small error is introduced here, in all probability, by the presence

of silica in the sample. A more serious source of error is that due to the presence of silicides, which are decomposed by the caustic soda solution. In analyzing commercial silico-carbides, the caustic soda solution is always found to contain an appreciable amount of aluminium, probably derived from the decomposition and solution of silicon-aluminium alloys. Strictly speaking, then, this method determines free silicon and silicon derived from certain alloys.

**Silica.**—The unattacked residue from the silicon determination is weighed and digested with hydrofluoric and sulphuric acids. When no further action is observed the excess of hydrofluoric acid is driven off by heating, the residue diluted with water, and the solution filtered off. The iron, aluminium, etc., are determined in the filtrate and the residue on the filter dried and weighed. The difference of the weights of the residue plus the iron aluminium, etc., and the original substance gives the silica present. According to Acheson siloxicon is slowly attacked by hydrofluoric acid, which would introduce a variable error into the determination. However, for technical work where the object is to determine the amount of carbon to be added to the silico-carbide, in order to avoid the formation of silicon, the method given has been found satisfactory.

**Combined Silicon.**—The residue from the silica determination is fused with a mixture of equal parts of sodium and potassium carbonates to which a little potassium nitrate is added. The fused mass is digested with water and the silica separated in the usual way, weighted and calculated to silicon.

**Combined Carbon.**—A weighed portion, about 0.3 gram, of the sample from which free carbon has been burnt off is mixed with about 8 grams of a mixture of calcined magnesia (1 part) and sodium peroxide (2 parts) in a nickel crucible. The weight of the magnesia and sodium peroxide mixture used must be known so as to correct for  $\text{CO}_2$  present, this being determined in a blank experiment. The crucible is then heated with a hydrogen flame until a vigorous reaction, accompanied by a considerable generation of heat occurs, which usually happens in less than a minute. The crucible is then transferred to a desiccator charged with soda-lime and allowed to cool, after which the  $\text{CO}_2$  is determined by any suitable means. After applying the correction for  $\text{CO}_2$  present in the magnesia and sodium peroxide mixture, the carbon in the sample may be calculated.

For most work it is not necessary to make all these determinations. It is simply necessary to determine free carbon, combined carbon, total silicon, metals. Then the oxygen present can be determined by difference. If, however, free silicon happens to be present it ought to be determined. The following example from actual practice illustrates the use of the analysis.

The silico-carbide gave the following analysis:

Carbon (free)	4.63
Carbon (combined)	21.48
Silicon (total)	58.03
Aluminium	4.21
Iron	1.52
Calcium	1.22
Oxygen (by difference)	8.91

100.00

The amount of silicon required by 21.48 grams of carbon to form  $\text{SiC}$  is 50.84. Subtracting this from 58.03 we have 7.19 grams of silicon which requires 8.10 grams of oxygen to form  $\text{SiO}_2$ . It is then assumed that 15.29 per cent of silica is present and to convert 15.29 grams of silica to silicon-carbide require 9.11 grams of carbon. But in 100 grams of the silico-carbide there are already 4.63 grams of free carbon, therefore the amount of carbon to be added is only 4.48 grams.

It is probably incorrect to assume that all the silicon not combined with carbon is present as silica; but the method used for calculating the proper amount of carbon to add to the silico-carbide in order to avoid the formation of silicon is found to give good results in practice.

If, for any purpose, it is desired to obtain very pure amorphous silicon-carbide, the commercial material, after burning off free carbon, must be repeatedly digested with hydrochloric acid. It is then repeatedly digested with hydrofluoric and nitric acids, followed by sulphuric acid. Finally, it is thoroughly washed with water. A sample prepared in this way gave the following analysis:

Silicon	69.41
Carbon	29.18
Iron and aluminium	0.59
	99.18

This corresponds closely to the theoretical composition of silicon-carbide. Taking the proportions of the silicon and carbon, we have:

	Found.	Theory.
Silicon	70.40	70.30
Carbon	29.60	29.70
	100.00	100.00

The substance might then be considered as nearly pure amorphous silicon-carbide.

#### COLLOIDAL PRECIPITATION UPON ALUMINIUM ANODES.

By WILLIAM ROY MOTT.

Engineers and inventors have repeatedly emphasized the importance of selecting the *proper electrolyte* for use with the aluminium electrolytic rectifier and condenser, and yet little has been done to answer the pertinent question: "What principles will guide us to new and 'better electrolytes?'" Other important questions present themselves. Why does an insulating film form? What is its exact composition? Why are nitrate solutions unsuitable? Why do films formed in citric acid resist even 500 volts? Why is film formed at 20 volts with sulphates several times thicker than a film formed at the same voltage with phosphates? An attempt will be made to answer these questions.

The mode of formation of the insulating film, its composition and chemical nature will here be considered in the light of the general phenomena of colloidal precipitation. Solutions of chromates, phosphates, tartrates, citrates, etc., strongly precipitate colloidal aluminium hydroxide. These same electrolytes produce insulating films upon aluminium anodes. These films also show absorptive phenomena similar to that observed in colloidal precipitation. These facts suggest that film formation at an aluminium anode and colloidal precipitation are closely allied phenomena. The first consideration is the composition of the film.

##### COMPOSITION OF THE FILM.

For a long time a great diversity of opinion has prevailed as regards the composition of the insulating film that forms upon aluminium anodes. Since the film formation occurs only with electrolytes producing oxygen at the anode, therefore this film has frequently been considered some oxide of aluminium. Since, however, different electrolytes produce films of vastly different character, a difference of composition in the film is expected with each electrolyte. For example, the film formed with sulphates, we may suppose to be basic aluminium sulphate, and that with phosphates, basic aluminium phosphate. To the generalization that the insulating film is always a basic salt, exception may be taken. For instance, distilled water has repeatedly been shown to cause high polarization of aluminium electrodes. For these and other reasons, we have to consider the following four possi-

ble compositions which have been ascribed to the film: (1) sub-oxide of aluminium, (2) oxide ( $\text{Al}_2\text{O}_3$ ) of aluminium, (3) hydrate of aluminium, and (4) basic salt of aluminium. The evidence for and against each of these theories will be briefly presented.

That the film is a sub-oxide of aluminium was proposed by Beetz (1866). First, Beetz proved that the film is not silicon. Buff (1857) had suggested this idea—plausible enough, in view of the large amount of silicon contained as an impurity in the aluminium. Next, Beetz attempted to show that the film is a sub-oxide of aluminium by the following method. The total coulombs passing through the electrolytic cell were measured by a silver voltameter. This current does work in three directions which were separately studied.

First, the changes in weight of the aluminium anode were determined.

Second, the aluminium dissolved from the electrode by the electrolyte (dil.  $\text{H}_2\text{SO}_4$ ) was determined by analysis.

Third, the oxygen gas liberated at the anode was collected and measured.

On adding up the electrochemical equivalent of the free and combined oxygen there was found a deficiency of 5 to 10 per cent. This deficiency Beetz explained as due to the formation of a film of sub-oxide of aluminium. However, the percentage of oxygen actually required for the film was small and well within the limits of experimental error! Wiedemann (1879) called attention to certain sources of error in Beetz's work. We may conclude, therefore, that, as yet, there is no real evidence in favor of sub-oxides or sub-salts of aluminium.

Oxide films were supposed by Faraday (1837) to explain the passive state of iron. Wheatstone (1855) and Heeren (1856) applied the same explanation to the behavior of aluminium electrodes in nitric acid and other electrolytes. That the film is oxide of aluminium has been the opinion of Planté (1859), Henrici (1864), Ducretet (1875), Ramann (1880), Neyreneuf (1888), Tommasina (1899), Fessenden (1899) and Cook (1904). Tommasina showed that a slightly oxidized aluminium electrode was the more luminescent in distilled water. Cook found that the coulombs required for forming the film apparently corresponded best with the idea of an oxide layer, but several losses were not investigated by him, and further in his most careful work he found the aluminium anode to weigh *more* than his theory required. Hence, we should look to the other two theories, the hydrate and basic salt.

Haagen (1897) calls the film a "hydroxide of aluminium." Lecher (1898) suggested an oxide film that changes over into a hydrate. He, however, says: "The explanation of the chemical part of the process is still surrounded with difficulties." The avidity for water is strong, so that only high temperature will dehydrate aluminium hydroxide. All analyses of films formed in aqueous solutions showed the presence of considerable water.<sup>1</sup>

But other substances are found in sufficient quantities, so that the film cannot accurately be called aluminium hydroxide.<sup>2</sup>

The oxide and hydrate theory have never been held as altogether satisfactory. Slouguinoff<sup>3</sup> (1878) was contented to

<sup>1</sup> The formation of an insulating film with fused electrolytes and the separation of metallic sodium in their neighborhood shows that water or hydroxyl is not always a necessary constituent of the film. An analysis of these films would be of considerable interest. See Carl Ham-buechen. "Trans. Am. Electrochem. Soc., 4, p. 106 (1908).

<sup>2</sup> Three hydrates of aluminium oxide,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  are known. Preference falls on  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; and this is plausible in view of Coasa's experiments (Il nuovo Cimentico (3), 3, p. 75, 228). The normal hydroxide is formed in transparent, iridescent laminae by bringing dilute aluminium amalgam in contact with a large amount of water. The hydrate,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , was obtained by Crum by drying at 100° his colloidal compound. Becquerel favored  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

<sup>3</sup> The work of this Russian scientist has been sadly neglected. Besides observing the iridescent, very hard films on aluminium anodes, he measured the high discharge potentials of aluminium and bismuth electrodes. Bismuth gave better results than aluminium. This is of interest in connection with Schonbein's observations upon the passivity of bismuth (Pogg. Ann., Vol. 43, p. 1, 1839), and it is also of interest as regards the high discharge potentials observed by Isenberg (1908) with lead electrodes. The capacity of these electrolytic condensers has not yet been measured.



say that the film consists of "aluminium oxide, hydrate or other aluminium compound." Jahn (1895) expressed his opinion that the insoluble film, formed on aluminium anodes in sulphate solutions, is "apparently of basic aluminium sulphate." Views of equivalent effect have been expressed by Raveau (1902) and Snowden (1904). We will now turn to the final test of the whole matter: The actual analysis of the anode film. This is the only conclusive test of its composition.

Becquerel (1861) published a valuable article entitled "Mémoire sur la production électrique de la silice et de l'alumine hydrates" (Memoir upon the electrical production of hydrates of silica and alumina). Thirty years prior to this time Becquerel had done work on the electrical production of mineral substances at low tension; but for this latter work, he used current at high tension. He obtained a deposit on aluminium anodes in potassium silicate solutions. He says, "It is remarkable to see a substance formed so rapidly acquire such extreme hardness." Then he reports the analysis made by M. Terreil and M. Fremy as follows:

Alumina	69.70
Silica	12.30
Water	18.00
	<hr/>
	100.00

Becquerel considered (aside from the silica) the anode product closely related to diasporé ( $\text{Al}_2\text{O}_3 + \text{H}_2\text{O}$ ).

Wilson (1898) separated the insulating film from the aluminium electrode by subjecting the same, immersed in mercury, to the electric current. This film was then analyzed by H. Jackson, who found it to be basic aluminium sulphate.

K. Norden (1899) detached the film in another way—by alternately using the aluminium as anode and then allowing it to stand in contact with the solution. Sufficient quantity of the film was obtained in this way to enable exact analysis to be made. The average of three experiments gave the following results:

	%
$\text{Al}_2\text{O}_3$	69.8
$\text{SO}_3$	13.2
$\text{H}_2\text{O}$	14.8
$\text{SiO}_2$	2.2
	<hr/>
	100.0

The author, by using aluminium foil as anode in sulphate solution has obtained sufficient of the film for analysis which showed a little more  $\text{SO}_3$  than Norden found.

These four independent analyses show conclusively that the insulating film consists of aluminium hydrates combined with basic salts of aluminium, or stating it another way: the film consists of aluminium oxide, water and acid radical.

For some time, the opinion has been advanced by Wilson and Norden that aluminium hydroxide is first formed and then this reacts with the electrolyte to take up the acid radical. It is first necessary to know if we can substitute an aluminium hydroxide film for the aluminium anode. This has been successfully done by Taylor and Inglis<sup>4</sup> who deposited aluminium hydroxide in the walls of a porous cup. With this membrane between platinum electrodes, they reproduced the peculiarities of the aluminium anode. The

conclusion is that aluminium hydroxide is first produced on the aluminium anode, and this reacts with the electrolyte. This phenomena of taking up acid radical is called adsorption.

#### ADSORPTION.

Aluminium hydroxide has strong affinity for adsorbing acid radical. This power is shown in colloidal precipitation, in ordinary precipitation and even in washing the precipitated hydroxide with electrolytes. The effect of adsorption upon the character of the film is important, as will be shown later.

The phenomenon of adsorption is a well-known characteristic of colloidal precipitation. The precipitated colloid (or coagulum) is always contaminated with portions of the precipitating electrolyte. In some cases the acid portion of the electrolyte is carried down; in others, the basic portion. The latter case is illustrated by the precipitation of colloidal solutions of  $\text{Sb}_2\text{S}_3$  and  $\text{As}_2\text{S}_3$ , which split off the metal or base of the electrolyte, and so leave free acid in the solution.<sup>5</sup>

The acid radical affects only slightly the precipitation of these colloids. Salts of trivalent metals (Al) precipitate these sulphides much better than salts of divalent metals (Ca, Zn, etc.), which in turn surpass in precipitating power salts of monovalent metals. This interesting effect of valence will be later applied to the aluminium anode phenomena; but with the difference that the *valence of the acid radical of the electrolyte is the important factor and not that of the metal or base.*

In ordinary precipitation of aluminium hydroxide by alkali hydroxide, trouble is experienced in precipitating aluminium hydroxide from solutions containing sulphates, silicates, etc. The hydroxide adsorbs the acid radical and so destroys the accuracy of the results. (Fresenius).

Patten<sup>6</sup> has determined by exact analysis this adsorptive power for a large number of metallic hydroxides in precipitation with potassium hydroxide. Curves are plotted by him showing the effect of the concentration of the alkaline solution. In the precipitation of alum<sup>7</sup> with four molecules of potassium hydroxide, the precipitate contains 24 per cent  $\text{SO}_3$  and 76 per cent  $\text{Al}_2\text{O}_3$ . The water content is not considered.

Ordinary precipitated aluminium hydroxide is used to purify alcohol, etc., because of its adsorptive powers. Warrington (1868) washed aluminium hydroxide with various solutions and found marked adsorption of the acid radical leaving the solution alkaline. Analysis showed the amount adsorbed to be greatest with carbonate, less with sulphates and least with nitrates and chlorides. In this order of electrolytes we find an analogy to the electrolytes that insulate the aluminium anode. Nitrates and halogen salts do not cause insulation. Sulphates are effective, but carbonates are better. Carbonates and sulphates contain divalent acid radicals, while nitrates are monovalent. This brings us again to the valence idea. But first, we would inquire as to what changes take place in the properties of the film due to this adsorption.

Aluminium hydroxide is precipitated by ammonia from a chloride solution in a loose, flocculent form which is easily soluble in hydrochloric acid and in alkalis. When this precipitate is left standing for a long time in contact with sulphate solutions, it becomes, as is well known, more and more insoluble in acids and even alkalis. This slow chemical process takes place with great rapidity at an aluminium anode. The loose, incoherent aluminium hydroxide is compacted together into a dense<sup>8</sup>, very hard, insoluble film of great specific resistance and high dielectric strength.<sup>9</sup> Sloughoff found that films formed slowly on aluminium anodes

<sup>4</sup> Taylor and Inglis regard the films as semi-permeable membranes that allow the so-called ions, H, Cl, Br,  $\text{NO}_3$ , etc., to freely diffuse through the films in the same selective way that sieving is done in a mill. The ions are supposed to be independent of each other and to squeeze through minute holes in the copper ferrocyanide or other membrane. The efficiency of the semi-permeable membranes, used in determining osmotic pressure, has been called in question by Quincke. (See Wied. Ann. 3, p. 621, 1902.) The author considers that mechanical sifting of ions does not explain the behavior of aluminium hydroxide films. The film forms a chemical compound with sulphur trioxide, which effectually stops further diffusion and at the same time changes the nature of the film. As in most cases, the compound is different in properties from its constituents.

<sup>5</sup> See Whitney and Ober. Jour. Am. Chem. Soc., 23, p. 857 (1901).

<sup>6</sup> See Am. Chem. J., 18, p. 608; Am. Chem. J., 25, p. 186 (1903).

<sup>7</sup> See "A Thermochemical Analysis of the Reaction Between Alum and Potassium Hydroxide," by Young. Am. Chem. J., 8, 23.

<sup>8</sup> The exact specific gravity of the film is quite important. See Dimensions of the Films, etc., ELECTROCHEMICAL INDUSTRY, July, 1904.

<sup>9</sup> See Electrical Properties of the Films, etc., ELECTROCHEMICAL INDUSTRY, September, 1904.

with sulphate solutions are so extremely hard<sup>10</sup> that they resist abrasion by emery paper. He also remarks upon the insolubility of the film in acids and even alkalis. But Beetz has shown that the film is sometimes soluble in alkali; he says: "The film, usually appearing with iridescent colors, dissolves easily in alkali." The author has shown<sup>11</sup> that the film does not prevent the *uniform corrosion* of aluminium by alkaline solutions—the reason being that the oxide and hydroxide of aluminium are soluble in alkali. However, this solvent action of alkali on the film is not altogether complete—a part of the film is not dissolved. Detached films show this very clearly.

Films have been detached by using formed aluminium plates as anode in copper sulphate solution (containing a trace of chloride). These detached films are insoluble in hydrochloric acid and in alkali. Films formed by using aluminium foil as anode were soluble to a certain extent in sodium hydroxide, but laminae of the insoluble portion remained unaffected for a long time in even concentrated potassium hydroxide.

The solidifying effect of different electrolytes will now be considered in detail.

#### VALENCE AND COLLOIDAL PRECIPITATION.

The effect of the valence of the precipitating part of the electrolyte has long been studied experimentally, and this has resulted in the discovery that the greater the valence the more powerful the precipitation. The law of this influence is not expressed by the usual  $1 : 2 : 3 : 4$  ratio, but by a logarithmic function<sup>12</sup> of the valence thus  $1 : x : x^2 : x^3$ .

If  $x = 32$  then the series becomes  $1 : 32 : 1024 : 32800$ . This corresponds to the power of monovalent, divalent, trivalent and tetravalent radicals.

Crum's (1854) very valuable work on colloidal aluminium hydroxide shows the importance of valence. He found that citric acid (trivalent) coagulates much more powerfully than tartaric acid (divalent) or sulphates. Chlorides and nitrates (monovalent) have one three-hundredths of the power of sulphates.

"Of the other acids which have been tried, the chromic molybdic, racemic, suberic, salicylic, benzoic, gallic, lactic, cinnamic, butyric, valerianic, carbozotic, camphoric, uric, meconic, cemenic and hemipinic acids all coagulate the solution; but their exact power has not been ascertained.

The acetic, formic, boracic, arsenious and cyanuric acids do not coagulate at least when moderately concentrated." The alkalis have less power than sulphates.

The above acids and their salts that coagulate colloidal aluminium hydroxide are proportionately efficient as electrolytes for forming an insulating film on aluminium anodes. To show how true this is, we shall briefly review the work done on the various electrolytes.

#### ELECTROLYTES.

The concentration of the electrolyte is usually of minor importance. Faraday's law demands that the amount of acid radical transferred to the anode for equal coulombs should be exactly the same, both for very dilute and for concentrated electrolytes. For this reason, the aluminium anode

generally behaves the same in concentrated as in dilute electrolytes. For similar reasons the basic portion of the salt is of minor importance.

Sulphate solutions were discovered by Buff and Planté to cause high polarization of aluminium anodes. Eichberg and Kallir (1898) found that concentrated<sup>13</sup> sulphuric acid is ineffective. Graetz (1896) enumerated soda-alum, potash-alum, dil. sulphuric acid, and alkali sulphates as suitable electrolytes. He observed a discharge potential of 22-25 volts. Guthe (1902) experimented with zinc sulphate and copper sulphate which behave much as other sulphates.

Chromate solutions were first used by Planté (1859). He lays great stress on the effectiveness of silver anodes for stopping the current with this electrolyte. Cail (1878) showed that solutions of chromates are much more effective than sulphate solutions. Battelli (1900) found that aluminium anodes polarize four times as fast with chromate solutions as with sulphates. Discharge voltages near 65 volts were measured. By using chromate solution containing a small amount of alkali, Pollak (1898) obtained critical voltages above 100 volts.

Carbonate solutions have been used successfully by several workers. Cail (1878) found them more effective than chromates or sulphates. Carl Liebenow (1898) used carbonate and bicarbonate of ammonia and later Siemens and Halske (1901) claimed that bicarbonates of calcium and magnesium are valuable electrolytes. Mitkiewicz (1901) used sodium carbonate solutions in his aluminium rectifier and condenser. The critical voltage with carbonates lies above 100 volts.

Alkaline solutions have been used, for example, ammonia, alkali aluminates, etc.

Silicates were used by Becquerel (1861) at high tensions with aluminium anodes. Polzenius (1899) observed a critical voltage of 120 volts with aluminium anodes in silicic acid. Borates are a class of electrolytes that Burgess<sup>14</sup> places above tartrates. Phosphate solutions have critical voltages in the neighborhood of 200 volts. Pollak, Polzenius, Nodon and numerous other experimenters have detailed work on the behavior of phosphate solutions.

Other inorganic electrolytes might be enumerated at length; but among organic electrolytes, there is a large number which are even more effective.

Pollak (1898) polarized an aluminium anode to the extent of 200 volts in a 5 per cent soap solution. Sodium potassium tartrate ( $\text{CHOH} \cdot \text{CO}_2\text{Na} \cdot \text{CO}_2\text{K}$ ) has been found effective by Andrews, Franchetti, Rypinski, Berti and others. Burgess and Hambuechen<sup>15</sup> give its critical voltage as near 200 volts at room temperature. Polzenius (1899) has shown, for organic compounds, that a peculiar ratio exists between the critical voltage and the size of the molecule and the number of carboxyl and hydroxyl groups; glycerine ( $\text{C}_3\text{H}_5(\text{OH})_3$ ) and sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) giving critical voltages of 40-50 volts, benzoic acid ( $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ ) nil, and citric acid ( $\text{C}_6\text{H}_7(\text{OH})(\text{CO}_2\text{H})_3$ ), 500 volts. Pollak claims that the organic acids and salts should contain in a molecule, two or more carboxyl groups ( $\text{CO}_2\text{H}$ ), or one or more carboxyl-groups, together with one or more hydroxyl, ketone or aldehyde groups. He cites as examples the acids, malic ( $\text{C}_4\text{H}_5(\text{CO}_2\text{H})_2$ ), tartaric, glyoxalic ( $\text{CHO} \cdot \text{CO}_2\text{H}$ ), phthalic ( $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ), salicylic ( $\text{C}_6\text{H}_4(\text{OH})(\text{CO}_2\text{H})$ ), and gallic. Siemens and Halske use salts of mandelic acid ( $\text{C}_8\text{H}_9\text{O}_3$ ) with success. The group of acids given by Crum as precipitating colloidal aluminium hydroxide nearly all belong to some one of the above classes which are effective electrolytes for producing high polarization of aluminium anodes.

The general influence of the valence of the acid radical on critical voltage is graphically shown in curve II. of Fig. 1. The abscissae give the valence of the acid radical; and the

<sup>10</sup> This property of the film reminds one of the precious stones, such as corundum, ruby and sapphire. A suggestion is made that they may be more closely related to our film than might be supposed.

<sup>11</sup> The Corrosion of Aluminium and its Prevention, ELECTROCHEMICAL INDUSTRY, April, 1904.

<sup>12</sup> Whetham (Phil Mag., 5, 49, p. 474, 1899) has neatly deduced the same result in a theoretical way. In the author's opinion, more stress should be laid on the chemical phenomena. Whetham postulates that a certain minimum charge be brought within reach of the colloidal group at a certain minimum frequency, in order that coagulation take place. For this conception the author would substitute that a certain minimum number of connecting bonds (or valences) should be brought within reach of the colloidal group at a certain minimum frequency. Then we shall get an equal number of connecting bonds (or valences) by 2n triads, 3n diads or 6n monads, where n is any whole number. The rest of the mathematical deductions follow from the theory of probabilities without change from Whetham's work. The conception of connecting bonds explains the netlike structure assigned to coagulums. It is easy to see that more strength of structure would result from the linking of colloidal groups with two triad atoms than three diad atoms.

<sup>13</sup> This result has been explained by Norden as due to its exceptionally strong solvent action upon aluminium hydroxide and oxide.

<sup>14</sup> Electrical Review, 44, p. 319, Feb. 27, 1904.

<sup>15</sup> Trans. Am. Electrochem. Soc., 1, p. 147 (1902).

ordinates represent the critical voltages on a logarithmic scale.

Monovalent acid radicals are quite ineffective either for causing insulation or for precipitating colloids. At the same time there is enough film formed to cause reduced single potentials<sup>18</sup> of an aluminium anode. Chlorates, thiocyanates, nitrates, acetates, formates, chlorides, fluorides, etc., belong to this class of inefficient electrolytes.

Sulphates, chromates, silicates, carbonates and numerous

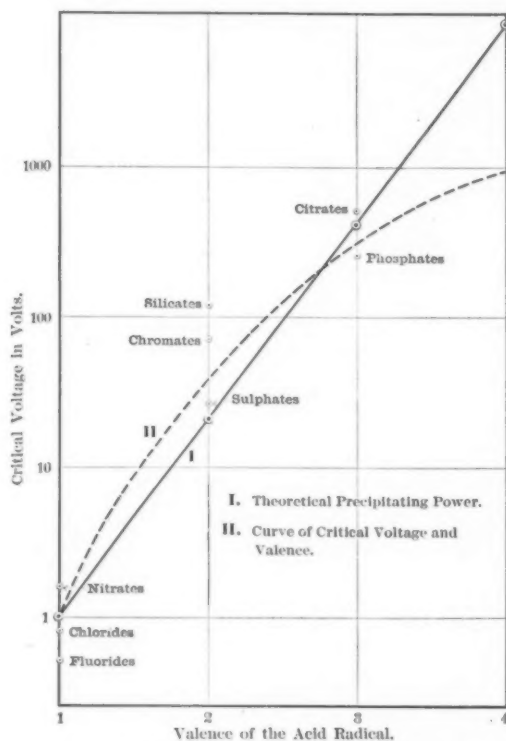


FIG. 1.—PRECIPITATING POWER OF SALTS WITH ACID RADICALS OF INCREASING VALENCE.

organic acids and salts represent divalent acid radicals which are effective electrolytes for producing insulation.

Acid radicals of higher valence are found among citrates, phosphates, antimonates, arsenates, borates, some silicates, some molybdates, some tungstates, etc., etc. Many of these have not been carefully studied as yet. It should also be remembered that in the case of a mixture of electrolytes the insulating power is that obtained with the least effective component of the mixture.

In curve I, is plotted the theoretical precipitating power of salts with acid radicals of increasing valence. The scale of ordinates is logarithmic, and in the units here used  $x = 20$  in the series  $1 : x : x^2 : x^3$ . This series has already been discussed as representing the law of increase in precipitating power of electrolytes of high valence.

The firmness with which the film is formed depends on the precipitating power of the electrolyte. With the increase in solidity comes a corresponding increase in the specific resistance of the film. For this reason, the specific resistance of films formed with phosphate solutions is over ten times greater than that of the films formed with sulphates.

#### SUMMARY.

Metallic aluminium (when free from the protecting film as in aluminium amalgam) reacts rapidly with water to form aluminium hydroxide. At an aluminium anode, chemical re-

action takes place according to Faraday's law between the electrolyte and the aluminium. The loose, incoherent aluminium hydroxide adsorbs acid radical by its great chemical affinity to form a very hard, dense, insoluble solid which possesses great insulating power. The necessary thickness of the insulating film varies with different electrolytes. Citric acid, trivalent, has extreme precipitating power and so films formed at 20 volts are much thinner than those formed in sulphates. This is typical. Electrolytes containing acid radicals of high valence give high critical voltages and films of great specific resistance and high dielectric strength, and so thinner films are obtained—thus less coulombs are required for the formation of the film.

This work is of practical importance. First, numerous new electrolytes are readily found, and second, their more important effects can be predicted. The suggestion is also made that some use may be found in qualitative analysis for phenomena described here.

#### OUR CHEMICAL INDUSTRIES AND HOW TO PROMOTE THEM

In a lecture held at the beginning of this year before the Drysalts Club, of New England, and recently published in pamphlet form, Dr. HUGO SCHWEITZER, the well-known Honorary Secretary of the New York Section of the Society of Chemical Industry, points out the enormous progress which the United States has made in recent years in the development of chemical industries. We lead to-day in the metallurgy of iron, copper, silver, aluminium and lead. Our supremacy is established in the petroleum industry, the refining of sugar, the manufacture of starch, glucose and paper. We produce more glass than any other country; we also excel in the manufacture of rubber goods, an industry born in the United States, and in the leather industry. We have developed the manufacture of water gas and originated illumination with acetylene gas. We are the largest producers of glue, lard, tallow and oleomargarine. Our manufacturers of sulphuric acid work to better advantage than their European competitors, and we supply almost as much acid as England, which produces the largest quantity. Our textile industries have grown to such an extent that we manufacture more silken wares than France and more cotton goods than England. Our woolen mills are the largest in the world. We are therefore justified in the general statement that the United States is the leading nation in chemical manufacture, as well as in other industries.

There are, however, some shortcomings in the chemical industries of this country. In 1900 we imported from Europe coal-tar colors and dyes, including alizarines, amounting to \$5,563,439, and fine chemicals, drugs, essential oils, amounting to \$6,530,037. Against these figures stand the following for domestic production: Artificial dye-stuffs, \$2,280,899; fine chemicals, drugs, essential oils \$4,206,744. It is only in some particular branches of chemical industry that stimulation is needed.

Dr. Schweitzer points out that it is not one thing or another that particularly stimulates the chemical industry, but a series of factors which are concerned in building it up, and which have resulted in making one European country, Germany, superior to the United States in the production of such chemicals as coal-tar derivatives, medicinal preparations, etc.

The various factors on which the developments of chemical industries depend are discussed one after the other by the author. They are: First, the occurrence in the country of the crude materials to be used as starting points in the chemical processes; secondly, the temperament of the nation, the natural bent of mind of the inhabitants; thirdly, the scientific and technical education of chemists; fourthly, proper co-operation of the government in enacting laws for the stimulation of the industry.

With respect to the second point, Dr. Schweitzer points

<sup>18</sup> See Burgess and Hambuechen, *ELECTROCHEMICAL INDUSTRY*, January, 1903.



out that Germans are inclined to slow, patient plodding, digging into difficult philosophical problems, while Americans desire quick results. For this reason, the United States is backward in the manufacture of coal-tar derivatives and fine chemicals, where the materials entering into the processes must pass through a long series of complicated, tedious reactions before the finished products are obtained. The importations of coal-tar colors in 1900 were \$5,563,439. This sum is distributed among about one thousand straight colors; that is, colors representing different chemical individuals. This means a manufacture of many compounds on a small scale. American color manufacturers occupy themselves with the production of a few dye-stuffs for which there is a large demand. The same aversion against working on a small scale is the reason that we still import fine silks from France and Germany and fine woolen goods from England and Germany. Our manufacturers could supply them as well as their European competitors, but they do not care to do so.

With respect to technical and scientific education, Dr. Schweitzer thinks that in this country it is most important to educate the capitalist and the employer of chemists, so far as they are not educated chemically themselves. The employer must be taught that he cannot expect immediate results from the working of the chemist. He must learn patience and let the chemist labor undisturbed. Give a chemist time and means to carry out his ideas and he will solve every practical problem put before him. The synthesis of indigo was a problem which it took about twenty years to solve.

The greatest part of Dr. Schweitzer's lecture deals with the problem of proper co-operation of the government in enacting laws for the stimulation of the industry. In this respect patent legislation is of great importance. The issuing of patents stimulates investigation and improvements, for, if they were not granted, processes and machinery would be worked in secret and industrial development would be delayed and hampered. Dr. Schweitzer thinks that the American patent laws are the best in the world. He answers to criticisms, sometimes directed against the principle of granting claims for products, while Germany grants claims for processes only.

"These critics do not consider that the protection of the process as granted by the German Government is much more valuable than the American process patent, for in the course of a litigation in Germany, the burden of the proof is not on the complainant, but, on the contrary, the party accused of infringement must show by legal evidence that he has committed no wrong. The accused party must admit expert witnesses to their works and prove that the patented process is not employed. According to our laws the burden of the proof is on the complainant, and he has to prove that his rights are injured by the defendant; and the latter can refuse admittance to his factory and state in his testimony that he considers his working process a business secret which he will not reveal. Under the circumstances you will readily see that a process claim in chemical patents affords hardly any protection in the United States, as everybody could infringe a process patent almost with impunity. I suspect that most of the critics of our patent system are advocating changes of our law because they want to be safe in infringing, to reap where they have not sown, and profit by other people's inventions and business abilities."

The lecturer then passed over to a discussion of the tariff question. There cannot be any doubt that it is due to our tariff laws that a number of new industries have been established in our country. Articles can now be manufactured here, owing to protective duties, the domestic production of which was formerly thought impossible. He quotes as an example the tin-plate industry.

In Dr. Schweitzer's opinion, however, our method of enacting tariff legislation is altogether unreasonable. The ques-

tions of dutiability are settled by a committee of the Senate and the House of Representatives, which finally in conference decide upon the context of any bill. "If we had a tariff commission composed of legislators, of prominent business men, of leading experts in the various lines of manufacture, and of men who make the study of national and social economics their specialty, we would get a tariff which would be just and equitable to all interests, and which would give an impetus to our industries greater than other means of stimulation. Such a committee should be permanent and empowered to act in emergencies."

If, for example, the time was ripe to begin the production of a certain article which could not be manufactured here before, interested parties could bring the matter before the committee and have the substance in question taken from the free list and put under protective duty. The author quotes, for example, oxalic acid. A reasonable protective duty levied on oxalic acid from now on would be of the greatest assistance to the American industry.

In every case, the duties levied should be protective, but not prohibitive. The amount of duty is assessed on three different principles—the specific duty, the ad valorem duty, and the compound duty, the latter being partly ad valorem and partly specific. In Dr. Schweitzer's opinion only specific duties should be levied on chemicals. However, it would be wrong to regard tariff laws a panacea for all evils of the industry, especially in chemical manufacturing. If it were so, we would find the most flourishing industry in the highest tariff countries. But this is not so, as shown by the example of Russia, with its high import duties.

"Closely related to the tariff is the inland revenue tax. In our country, chemical manufacture is only affected by the tax levied on alcohol. It cannot be denied that this tax most seriously injures chemical manufacture. Alcohol is practically indispensable in our industry, and, although American chemists, forced by the great expense, introduced substitutes in the form of wood alcohol, acetone and other organic solvents, in some branches of manufacture, alcohol still remains a *sine qua non* in the majority of cases. If we were called upon to give an instance of a "blood tax" we would point out the internal revenue tax on alcohol for manufacturing purposes, and for this reason: sulphuric ether is one of the most important derivatives of grain alcohol, which must necessarily be employed in its manufacture.

"Ether is most extensively employed as an anæsthetic in surgical operations, and the enormous consumption of ether in the United States becomes apparent by the fact that one New York hospital alone used 2900 pounds last year. The price for ether is 70 cents per pound, whereas in Germany the same quality, made from tax-free alcohol, is sold for 7½ cents per pound. Although Germany levies a very heavy internal revenue tax on alcohol as a beverage, it allows tax-free alcohol for manufacturing. It has introduced for this purpose the system of denaturalization, which means rendering the alcohol unfit for drinking by the addition of various ingredients. Above all, wood alcohol and pyridine, a substance derived from the tar obtained in charring bones, are mixed with the alcohol in such a manner that recovery of grain alcohol from the mixture is practically impossible. For uses in the various industries different methods of denaturalization are adopted. Because the ordinary mixture is ill-smelling on account of the presence of pyridine, it cannot be employed for the manufacture of perfumery. Therefore, the wise government allows for this use a different manner of denaturalization which eliminates pyridine, and whenever a manufacturer proves that the ordinary tax-free alcohol is not fit for making his specialties, on account of the presence of these chemicals, another form of denaturalization is devised and permitted. In the same manner, Germany permits the denaturalization of salt, on which it levies a revenue tax when used for eating purposes. As well known, salt is largely employed in the dye-

stuff industry for the precipitation of dyes from their watery solution. Salt is therefore denaturalized by coloring it with dye-stuffs, and it is a curious sight in German factories to see in the yards heaps of blue, yellow, green and red salt which are employed for the precipitation of the corresponding coloring matters."

Owing to the tax on alcohol a number of articles cannot be manufactured here at all, and must be imported. Among them are fulminating powders and fulminates. "It is absolutely imperative for our Government to follow the example of Germany, if we wish to see the manufacture of fine chemicals as flourishing here as it is there."

Dr. Schweitzer finally refers to another class of legislation as a great promoter of chemical industries which at first glance appears to be much more oppressive than beneficial. These are the laws for preventing such nuisances as fouling the air and polluting water courses.

"In the early eighties the municipal authorities of some towns in the zinc mining district of Silesia passed legislation against the escape of sulphurous acid gas from the chimneys of the roasting furnaces of zinc ores. Chemists in the employ of the zinc smelters undertook the task of finding some uses for the generated gas, which at that time was practically valueless. They succeeded in compressing the gas to a liquid on a commercial scale and used it in processes invented by themselves for the manufacture of glue and gelatine. But the supply of gas from the roasting furnaces became soon so enormous that they had to find still other uses. It then occurred to them to attempt the oxidation of sulphurous acid by means of the oxygen of the air for the production of sulphuric acid, a reaction which had been scientifically exploited by the famous chemist Clemens Winkler. Their experiments were successful, and soon they established works where sulphuric acid was manufactured from sulphurous acid gas, which hitherto escaped as a useless by-product, in roasting zinc and iron pyrites, vitiating the air and destroying vegetation. In this manner was born what we call the contact process for the manufacture of sulphuric acid, which, with later improvements by other investigators, revolutionized a branch of chemical industry in which it was generally believed that there was hardly any room for improvement.\* In this connection let me add that this contact process is one of the factors which made the synthesis of indigo a commercial success. One of the steps in the process of making this color is the oxidation of naphthalene by means of fuming sulphuric acid, the decomposition of the latter producing sulphurous acid. Instead of allowing the gas to escape it is now treated with the oxygen of the air in the contact process, reconverted into sulphuric acid, which enters again into the circle of the indigo synthesis.

"Another example we find in the starch industries. Until the manufacturers were prevented from running their wastes into rivers they made only starch and products derived therefrom. But when the law prohibited the pollution of water courses they investigated what they formerly called waste, and found that it contained valuable albuminoid matter, which is now utilized as feed; that an oily substance which formerly escaped their notice was present in the waste which could be extracted and employed for the manufacture of soap and glycerine, and by treatment with sulphur could be transformed into a substitute for rubber.

"An interesting example, is also the following: In the preparation of sauerkraut a juice is pressed out from cabbage which contains decomposed vegetable matters, and when run into rivers kills the fish in the water. It was therefore forbidden to pollute water in this manner. Then chemical research established the presence of valuable organic acid in this waste water, and by concentration and filtration a liquor was obtained which proved to be of great value in the textile

industries and in the tanning of skins. This liquid is now in the market under the name of 'Vegetalin.'" (Concerning the "sauerkraut industry," Dr. Schweitzer remarks that there are alone on Long Island about twenty factories, each using every season 2,500,000 pounds of cabbage, which furnish 80,000 gallons of juice as a by-product, or 1,500,000 gallons of waste in the Long Island factories alone. Around Chicago and St. Louis there are still larger establishments.)

The author thinks that if there is anything which fosters chemical manufacture in Germany, it is the intelligent co-operation of the government with the manufacturing interests and with the educational elements. "In this respect our strenuous republic has still something to learn from what many of us are apt to consider an effete monarchy."

### THE MANUFACTURE OF FERRO-ALLOYS IN THE ELECTRIC FURNACE.

By GEORGE P. SCHOLL, PH. D.

(Concluded from page 396.)

The ferro-silicon obtained in the electric furnace comes directly into competition with the alloy made for a long number of years in the blast furnace, running the latter with a very refractory slag and at a very high temperature, and a consequent excessive consumption of fuel. A silicon content of 15 per cent, however, is about the highest which can be reached in the blast furnace, owing to its temperature limits and the infusibility of the slag. The peculiar adaptability of the electric furnace, however, to various temperature requirements, made it eminently suitable for the production of alloys with a higher silicon content, and products ranging from 25 per cent all the way up to 80 per cent are readily obtained. They are well fused and taken altogether represent a more homogeneous material than that obtained by the old method. Naturally, a considerable amount of missionary work had to be done to get consumers accustomed to the use of the higher grades of alloys, which was all the harder, as the product obtained in the early stages of manufacturing was sometimes disappointing in the results obtained by it. The advantages, however, resulting from their use, are more and more appreciated and their employment will undoubtedly be much extended in the not far distant future. The advantages accompanying the use of the high-grade alloys in the iron and steel industry, have been set forth at some length in *ELECTROCHEMICAL INDUSTRY*, vol. II., page 122, and will therefore not be detailed here. The tendency is toward the employment of the higher grades, corroboration of which, as far as the German steel works are concerned, is furnished by a statement of Dujardin, to the effect that at present the employment of 25 per cent ferro-silicon seems to be completely abandoned by them, the 50 per cent alloy being more and more in demand. From 10 tons in the second half year of 1902, the consumption of the latter alloy increased to about 500 tons in the second half year of 1903, which fact certainly bears testimony to the success which has attended its application in practice. The alloy, owing to its porous structure, is easily gotten into the shape of a coarse powder, of about nut size, and is used as such directly in the ladle. Dujardin also states that the 75 per cent Si alloy is still too expensive to be used for general purposes, but that, when well made, it is easily incorporated into the molten steel, the reaction is very rapid and energetic, and that whenever the day arrives when it is no more expensive per unit of silicon than the 50 per cent alloy, it will be universally preferred.

As far as the manufacture of ferro-silicons, with varying per centages of silicon, is concerned, the energy expended increases, of course, considerably the richer the alloy is in silicon. All things considered, from an economic standpoint, as pointed out by Keller in his *Iron and Steel Institute paper* (I. c.), the manufacture on a large scale of alloys rich in silicon is cheaper per unit of silicon the

\* In this connection an article in our September issue (page 347) should be of interest.—Ed.

higher the percentage of the latter in the alloy. This is explained by the fact, that in the low-grade alloys the price of the iron is the most important item, while it becomes much less important in the higher alloys, being replaced there by the much cheaper silica. The purity of the product is also greater in the higher alloys, inasmuch as the impurities are almost exclusively introduced by the iron used. Furthermore, the manufacture of the higher alloys demands a greater and more prolonged application of heat, thus favoring the elimination of impurities by volatilization or secondary reactions.

A sort of a scare has lately been created in the mind of the public by the reports of explosions of ferro-silicon made in the electric furnace, while being handled in a warehouse in Liverpool. This occurrence has even been deemed of sufficient importance to be made the subject of papers before the recent meeting of the British Iron and Steel Institute and the Faraday Society. The alloy in question came from Trieste and had the following composition: Si = 59.40, Fe = 36.85, Mn = 0.08, Al = 2.73, Ca = 0.14, Mg = 0.17, C = 0.218, S = trace, P = 0.056. It was concluded that the explosions were probably due to the presence of impurities, more particularly the phosphorus, and it was recommended to the manufacturers to in future only use such materials as are free of phosphorus. Prof. Le Chatelier, however, the well-known French metallurgist, pointed out in the discussion to the paper before the Iron and Steel Institute, that the theory of the explosions having been caused by an evolution of phosphoretted hydrogen hardly seems plausible, as the percentage of phosphorus as so low, and as its presence is carefully avoided in the manufacture of ferro-silicon, as well as in that of calcium carbide. He believes it much more likely that the explosions are to be attributed to silicuretted hydrogen, one of the modifications of which is spontaneously inflammable. He states that silicide of calcium is unavoidably found at times, when ferro-silicon is manufactured in the same furnace as has been used for the manufacture of calcium carbide, that appreciable masses of it are often present in commercial calcium carbide, and that under the action of acids it instantly yields spontaneously inflammable silicuretted hydrogen. The calcium silicide is not equally distributed throughout the mass, and a batch of ferro-silicon made immediately after a calcium carbide burden, would probably be contaminated. The above opinion of Prof. Le Chatelier appears undoubtedly the correct one, and it seems the casting of doubt on the product of the whole industry was certainly unwarranted, inasmuch as the greater part of the production of some 5000 tons annually is made in furnaces which are not used for carbide.

#### FERRO-CHROMIUM.

This alloy, like ferro-silicon, was one of the pioneer products of the electric furnace, when the latter was applied to the manufacture of the ferro-alloys, and as outlined above, its manufacture underwent a gradual evolution as far as quality of the product was concerned, after passing through a period of ruinous competition.

The manufacture of the alloy can be carried on either in the blast furnace, the crucible furnace or the electric furnace, and was in former years carried out almost exclusively in the blast furnace. The latter, however, does not furnish an alloy richer in chromium than 30 to 40 per cent, and is probably now entirely out of the race, as the preference among consumers is given to a material containing at least 60 per cent. The manufacture in the crucible furnishes alloys of high percentage, but only small quantities of material can be treated at one time, special and expensive crucibles are required and the impurities contained in the alloy are rather high. The electric furnace is therefore the only means by which alloys of a high percentage of chromium can be manufactured in a sufficiently pure state and in sufficiently large quantities for commercial use. Large quantities of ferro-chromium are manufactured by the aid of electricity, especially in this country,

France and Germany, among them rich alloys of very high purity, especially in regard to the amount of carbon, which they contain.

The manufacture of the alloy is carried on in a variety of furnace constructions, from the simple furnace, as used among others by Willson, where the crucible constitutes one of the electrodes to the more complicated forms employed in Europe, where the electrodes do not come into contact with the alloy. Some data on the manufacture of ferro-chromium in this country by the Willson Aluminium Company at Kanawha Falls, W. Va., and Holcomb Rock, Va., are given by Dr. Haber in his report, mentioned above (l. c.). According to him the works at Kanawha Falls use three dynamos of 800 kw. each, those at Holcomb Rock one-third of that power. The ore used is principally Cuban and Turkish chrome iron ore, Canadian and New Caledonian ore being also employed. The Cuban ore has the following composition:  $\text{Cr}_2\text{O}_3$  = 50 per cent,  $\text{FeO}$  = 18.57 per cent,  $\text{Al}_2\text{O}_3$  = 12.44 per cent,  $\text{MgO}$  = 13.38 per cent,  $\text{CaO}$  = 2.16 per cent,  $\text{SiO}_2$  = 3.82 per cent, S = 0.69 per cent, P = 0.2 per cent. The Turkish ore analyzes:  $\text{Cr}_2\text{O}_3$  = 52.8 per cent,  $\text{FeO}$  = 10.24 per cent,  $\text{Al}_2\text{O}_3$  = 10.48 per cent,  $\text{MgO}$  = 13.96 per cent,  $\text{CaO}$  = 2.37 per cent,  $\text{SiO}_2$  = 6.95 per cent, S = 0.06 per cent, and  $\text{Fe}_2\text{O}_3$  = 3.79 per cent. The ferro-chromium obtained shows Cr = 70.96 per cent, Fe = 23.23 per cent, Si = 0.5 per cent, C = 5.21 per cent, P = 0.008 per cent, and S = 0.078 per cent, the consumption of energy being about 10.6 e. h. p. hours per kilogram of the product. Alternating current of 110 volts pressure is used at Kanawha Falls, the current of 22,000 amperes being divided on seven furnaces, all of them crucible furnaces of partly circular, partly square and rectangular cross-section. The outside dimensions of the largest furnace are 120 inches wide, 80 inches long and 60 inches high, the smaller ones being about 60 inches square and 50 inches high. The furnaces are iron boxes, with a very thick lining of pieces of anode carbons, with a tar binder. They are provided with a tapping hole. In a few furnaces the lining constitutes one electrode, while the other electrode is formed by a bar of carbon, which depends vertically into the furnace. Other furnaces have two parallel electrodes, which depend vertically into the crucible and are movable. In this latter form the crucible itself is not connected into the electric circuit. The hanging electrodes are in each case bars of 60 inches in length and 4 x 4 inches cross-section, two bars laying side by side forming one electrode. The iron heads into which these electrodes are fastened, are provided with cooling arrangements by means of water. The carbon lining is stated to be replaced in time totally by the material of the melt, which is constantly produced in the furnace, so that finally the melting takes place in a crucible practically of the same material as that which is melted.

Ferro-silicon and ferro-chromium are made at Livet, according to the report of the Canadian Government Commission sent to France to investigate the possibilities of the electric furnace for the manufacture of iron (ELECTROCHEMICAL INDUSTRY, Vol. II., page 180), in a furnace closely resembling the one illustrated above, except that the base of each shaft is formed by a carbon block, which blocks are in electrical communication on the outside of the furnace by means of copper bars. The carbon electrodes which depend into each shaft are 28 inches in diameter and 53 inches long.

According to Pitaral, the works manufacturing ferro-chromium in France are the following: Société Electrometallurgique Française at La Praz, Société La Néo-Métallurgie at Giffre, Société Anonyme Electrometallurgique at Albertville, Keller, Leleux & Co. at Livet, Société Electrometallurgique de Saint-Béron at Saint-Béron, Ch. Betrolus at Bellegarde and Rochette Frères at Epierre. From the statement of Dujardin mentioned above, it appears that the products of the French works are somewhat lower in carbon than that which is given in the analysis of Wilson's product quoted above. Within recent



times a soft ferro-chromium (ferro-chrome doux) has been put on the market, especially by the Société la Néo-Métallurgie, containing carbon as low as .25 per cent. This latter alloy is much appreciated, but on account of its high price its use is as yet rather limited. Its price is quoted at Paris as 4 francs per kilogram, based on a percentage of 60 of chromium and 0.4 to 1 per cent of carbon, with increase of 0.06 francs for every unit of chromium above 60 per cent. The Société la Néo-Métallurgie has also patented a ferro-chromo-nickel alloy of the following per centage: 16-38 per cent Fe, 5 to 60 per cent Ni and 24 to 57 per cent Cr. The total combined amount of the three metals is 98.80 to 99.50 per cent, and the alloy contains from 0.30 to 0.80 per cent of carbon, the rest being made up of silicon, sulphur and phosphorus. A ferro-chromo-silicon, containing 50 per cent of chromium, 8 to 10 per cent of silicon, 38 per cent of iron and 2 per cent of carbon is also quoted regularly at 650 francs per ton.

#### FERRO-MANGANESE.

Ferro-Manganese is another one of the alloys, which were the first ones to be made in the electric furnace, and the hopes entertained about its manufacture were rather sanguine. These hopes were, however, doomed to disappointment, and at the present time, according to Pitaval (*Journal de l'Electrolyse*, page 4, 1904) the manufacture of ferro-manganese in the electric furnace has been abandoned in France. A great deal of trouble has been experienced in the manufacture of this alloy in the electric furnace, due principally to the absolute necessity of avoiding too high a temperature with consequent great volatilization of the manganese and very low yield. The blast furnace, which has been so effectively attacked by the electric furnace, as far as ferro-chromium and ferro-silicon were concerned, still reigns supreme in the field of ferro-manganese, on account of the more economic production possible. A silico spiegel, however, with 20 to 25 per cent of silicon and 55 to 40 per cent of manganese, or 50 per cent of silicon and 30 per cent of manganese is reported to be manufactured by Keller, Leleux and Co. at Livet. A mangano silicon, with about 76 per cent of manganese, about 21 per cent of silicon, about 1 per cent of iron and about .95 per cent of carbon is also quoted.

#### FERRO-TUNGSTEN.

The reduction of this alloy cannot be performed in the blast furnace on account of the high temperature necessary. The alloy made in the electric furnace by reducing tungsten concentrates has to compete against the metallic tungsten in powdered form, as it is furnished by the chemical works. It seems that its manufacture is principally carried out at the Albertville works, the manager of which, M. Girod, claims to have melted an alloy of 85 per cent tungsten in his furnace described by Bennie in *ELECTROCHEMICAL INDUSTRY*, Vol. II., page 309. The purity of the product in regard to the contents of carbon, has been much improved. In Germany it is said to be little used as yet, as the tool steel manufacturers prefer the powder. Nevertheless, the use of the alloy is likely to increase, as it is claimed that the alloy has the following advantages: 1. It alloys easily with the steel and almost quantitatively, without loss, while the metallic powder oxidizes more easily and is very refractory. 2. A good ferro-tungsten obtained in the electric furnace contains generally less impurities than the powder. 3. The unit of tungsten in the ferro-alloy costs much less than that in the powder. Alloys made in the electric furnace showed the following composition: Tungsten, 70-75 per cent, carbon 2-3 per cent, sulphur and phosphorous less than 0.02 per cent; tungsten about 80 per cent, carbon 1.5-2 per cent; tungsten 80 per cent, carbon 0.52 per cent, silicon 0.1-0.2 per cent, sulphur and phosphorous almost nil, the total impurities less than 0.75 per cent. The latter alloy is, of course, a very fine product. The 70 to 80 per cent alloy is quoted in Paris at 4 francs per unit.

The analysis of ferro-tungsten manufactured at Kanawha Falls is given by Haber (l. c.) as 60.92 per cent of tungsten,

28.38 per cent of iron, 0.566 per cent of silicon, and 2.36 per cent of chromium. Rossi (*Mineral Industry*, 1903, page 695), dealing with his method of the reduction of oxides by aluminium in the electric furnace, states that for the manufacture of ferro-tungsten he used concentrates of the following composition: Tungstic acid 69.86 per cent, silica 5.04 per cent, ferrous oxide 20.25 per cent, equivalent to 55.20 per cent of metallic tungsten and 15.73 per cent metallic iron. A furnace of the old Siemens type, consisting of graphite blocks with a central cavity, serving as cathode and a vertical, movable carbon anode, was charged with ingots, scraps, etc., of aluminium in sufficient quantity to reduce the iron and the tungsten. The current was then allowed to melt the aluminium and the oxides were introduced into the molten metal. The reaction began at once, the iron being first reduced to metal and forming a bath in which the tungsten dissolved. Abundant fumes of alumina in a dense white cloud were given off as the reaction proceeded, while the larger portion of the alumina formed a sort of slag on the surface of the bath. The current was increased towards the end of the reaction for a few minutes and the metal was then cast. With the expenditure of about 11 hp. of current, 646 pounds of an alloy containing 75.91 per cent of tungsten, 21.47 per cent of iron, 161 per cent of silicon, 0.08 per cent of sulphur, 0.90 per cent of carbon and no aluminium are stated to have been made in 30 minutes.

#### FERRO-VANADIUM.

There is still a good deal of controversy about the use of this alloy in metallurgical circles, as the influence of vanadium on iron and steel products has not been definitely ascertained yet. Ferro-vanadium alloys, when they were first manufactured were far from pure, inasmuch as they contained about 5 to 10 per cent of aluminium and 2 to 3 per cent of carbon. It has been possible, however, lately to put products on the market, the analysis of which showed 26.25 per cent of vanadium, 73 per cent of iron, 0.40 per cent of aluminium, traces of carbon and 1.0 per cent of silicon. The prices for the 25 per cent alloy, guaranteed free from carbon, as given some time ago by the Syndicat International du Vanadium at Paris, were 20 francs per kilogram in quantities from 1 to 20 kilos, going down to 16 francs per kilogram for ton lots and above. A ferro-silico vanadium has also been prepared in somewhat larger quantities, which contained 30 per cent of vanadium, 10 per cent of silicon and 2 per cent of carbon. It is claimed that on account of the silicon which it contains it has the great advantage to elevate the temperature of the vanadium which it accompanies into the bath of the metal, with which it is to be alloyed, and to aid the smallest quantities of the vanadium to distribute themselves evenly through the bath. The silicon besides has the advantage of preventing high percentages of carbon. Gin, the well-known French electrometallurgist, has lately patented an electrolytic method for the production of ferro-vanadium, which is described by the writer in *ELECTROCHEMICAL INDUSTRY*, Vol. II., page 324. It depends upon the electrolysis of vanadium fluoride dissolved in calcium fluoride, the cathode being a bath of liquid iron, and the anode a specially prepared and compressed mixture of vanadium trioxide and carbon. The fluorine produced by the electrolysis of the vanadium fluoride dissolves the vanadium compound of the anode and regenerates the electrolyte, while the vanadium alloys with the iron. Gin states that for alloys with more than 25 per cent of vanadium the cathode section should be appreciably less than the active anode surface. Good results and a sufficiently liquid bath are stated to have been obtained with a medium current density of two amperes per square cm. of active anode surface, six amperes per square cm. cathode surface, and between eleven and twelve volts pressure. Data as to the working of the process on a large scale in practice are not available.

#### FERRO-MOLYBDENUM.

This alloy is made at the Albertville works, and at the

works of the Néo-Métallurgie Society at Rochefort sur Mayenne. It is said to be little used in Germany, the consumers preferring the metal. The alloy most generally used contains about 60 per cent of molybdenum, the prices at works being quoted as 19 francs per kilogram of molybdenum for the 60 to 80 per cent molybdenum alloy, containing two to three per cent of carbon. The sulphur and the phosphorous are each below 0.3 per cent. Rossi states that by the use of his process he has obtained the alloy free from carbon.

#### FERRO-TITANIUM.

It is unnecessary to dwell on the manufacture of this alloy in the electric furnace, inasmuch as it has been discussed at considerable detail by Rossi in *ELECTROCHEMICAL INDUSTRY*, Vol. I., page 523, who has made a special study of the alloy for a number of years, and has contributed much to our knowledge on the subject.

In the foregoing the uses of the different ferro-alloys dealt with and the properties which they impart to the products with which they are incorporated have not been considered, as they are briefly and concisely stated in an extended extract from an article by Rossi in the *Iron Age* of November 12, 1903, in the Synopsis of Articles in Other Journals, *ELECTROCHEMICAL INDUSTRY*, Vol. I., page 583.

In concluding this brief review it is hardly necessary, in view of the facts pointed out above, to assert that the electric furnace has established its right to be considered an important adjunct in metallurgical practice and that the time is over definitely when it could be looked upon as a mere laboratory toy of doubtful practical ability. The high temperature which can be obtained in it, the ease with which it can be regulated, and the consequent possibility of successfully handling refractory substances beyond the limit of ordinary furnaces, are advantages which are making themselves felt more and more. Signs are everywhere apparent which indicate that the time is fast approaching when it will be utilized to a much larger extent in metallurgy than at present. All honor is therefore due to the pioneers in the manufacture of the ferro-alloys, who, recognizing its possibilities, labored hard and in the face of serious and discouraging obstacles, to demonstrate its practical applicability.

#### WILHELM OSTWALD.

In a review of P. Walden's biography of Wilhelm Ostwald, Dr. WILDER D. BANCROFT writes in the October issue of the *Journal of Physical Chemistry* as follows:

"The change in the scientific status of Ostwald has been a remarkable one. In 1890 the electrolytic dissociation was fighting for recognition. Nernst's paper on the voltaic cell had been published, but had attracted very little attention. The general feeling of chemists toward Ostwald was that he was an able man who was wasting his talents. Some went so far as to deny his claim to being a chemist. Any idea held by Ostwald was *per se* an object of suspicion. To-day the opposition to the electrolytic dissociation theory comes from those who believe that it has outlived its usefulness. Ostwald is recognized as one of the leading chemists of the world, and any opinion of his is promptly accepted as dogma by a large enthusiastic following.

"Ostwald is essentially a leader of men. The theory of solutions was furnished by Van't Hoff; the theory of electrolytic dissociation by Arrhenius; the theory of the voltaic cell by Nernst. Not one of these three important generalizations is due to Ostwald; but he has taken all three, developed them and brought them to recognition and acceptance as no one else could have done. Nernst's theory of the voltaic cell lay dead until Ostwald took it up. Everything about the theory of electrolytic dissociation except the formulation is due to Ostwald. No one believes that Arrhenius could have overcome

the opposition of the chemists. It was Ostwald who brought the theory of osmotic pressure to the front. The work of the Beckmann, done in Ostwald's laboratory, made the testing of the theory a simple matter, while Ostwald himself lost no opportunity to impress people with the importance of the theory.

"It is a leader rather than as a pioneer that we must consider Ostwald. The pioneer discovers the new land; but his discovery will come to nothing if the people do not follow him and take possession of the country. The pioneer is independent of the world. He must have a clear insight and courage. The leader must not be too far ahead of his followers. He must be working toward the same goal as they and be able to help them forward. He is handicapped by the fact that he cannot move faster than the army can follow him, but this is more than balanced by the fact that every advance is held.

"To some it has seemed that Ostwald's point of view has not changed in the last ten years as much as it should have done. This may or may not be true. It is true, however, that the chemical world has been brought up to Ostwald's position by Ostwald; and there are a few who hope and believe that Ostwald's Faraday lecture is the signal for a new and rapid advance. It may well be so. For seventeen years, the bulk of the work in physical chemistry has been devoted to dilute solutions, largely as a result of Ostwald's personal influence. So great is his influence that he could change this inside of a twelve-month. Ostwald exerts a tremendous power in the chemical world to-day. If he will devote himself to chemistry instead of to philosophy, and will throw his influence in favor of progress, there is before him another era of triumphant achievement, compared to which the results of the past decade will appear trivial. If he does not do this, the world will still move on, though not so rapidly as might have been the case."

Prof. Ostwald's Faraday lecture, to which reference is made above, deals with the same ideas which were brought forward by him in his Bunsen Society paper on hylotropy abstracted on page 361 of our September issue.

#### SOME EXAMPLES OF CATALYTIC ACTION IN ELECTROLYSIS.

By C. J. THATCHER, PH. D.

It has been emphasized in this and other journals recently, that in all electrolyses on polarizable electrodes it is advantageous to very carefully control the e. m. f., not only of the entire cell, but more especially of the anode or cathode, or both, as the case may be. This subject is not without a bearing on commercial electrolyses, for wherever secondary and usually undesirable electrode processes can occur—and that is quite generally—their velocity will be influenced among other things by the e. m. f. of the concerned electrode. For this reason, the control of the e. m. f. of polarization is an important factor in increasing current yield.

Among other papers bearing on this subject is that recently presented at the International Electrical Congress by Prof. W. Ostwald, of Leipzig University, and which was published in the October number of this journal. Prof. Ostwald draws attention there to the fact that with increasing e. m. f. applied to the terminals of the cell those ionic processes will first occur which require the smallest difference of potential. He also points out some of the factors, other than applied e. m. f., which will influence the electrode e. m. f. or polarization. Of these ionic concentration, diffusion rates, induced and purely chemical reactions and catalytic influences may be mentioned.

It is desired here to treat especially of catalytic influences in electrode processes, and to illustrate them by some concrete examples. Most of those to be mentioned were observed during the course of an extended investigation of an electrolytic oxidation process made in Prof. Ostwald's laboratory in Leip-

zig in the years 1901-1903 and published in the *Zeit. f. Phys. Chemie.*<sup>1</sup> During this research certain observed phenomena impelled the author to contend that catalytic influences played an important part in this and other electrode processes. And by means to be given in part here, he was able to verify this theory and to bring to Prof. Ostwald's attention the ideas of catalytic electrode influences to which he has given expression in the above-mentioned paper, and which Prof. Luther and his scholars are now further investigating.

It is unnecessary to review the general aspects of the subject, for Prof. Ostwald has shown in his paper how catalytic agents may be expected to act in electrode processes. He has also pointed out in what direction the idea may be applied practically; that is, namely, first, in synthetic work to retard undesirable reactions by the use of negative catalyzers, or to accelerate such as are desired with positive catalyzers; and, secondly, to analyze electrode processes in order to arrive at the mechanism of any process under investigation.

These two applications are well illustrated by the effect of catalytic agents in the oxidation of sodium thiosulphate solutions on platinized platinum anodes, which was investigated by the author in the before-mentioned research. For the sake of clearness it will be necessary to state here briefly some of the results of this investigation. It was found that solutions of C. P. recrystallized  $\text{Na}_2\text{S}_2\text{O}_3$  in purest redistilled water are very slightly alkaline—as is not generally known. This alkalinity can be ascribed to several causes which it will not be necessary to give here. As long as this weak alkalinity of the solution was preserved, the result of the electrolytic oxidation was the formation of sodium tetrathionate— $\text{Na}_2\text{S}_4\text{O}_6$ —in almost theoretical quantities. In this case the solution remained very nearly neutral throughout the electrolysis. The tetrathionate ion itself was not further oxidizable at any anodic polarization, however high. But in solutions which contained any considerable amount of alkali, it was established that the  $\text{S}_2\text{O}_3$  ion was slowly decomposed by hydrolysis forming among other substances trithionate, and that this was then further oxidized to sulphate. In acid solutions, on the other hand, the  $\text{S}_2\text{O}_3$  ion was slowly decomposed by hydrolysis forming among sulphite, which latter was oxidized at once to sulphate. The primary electrode process in thiosulphate oxidation proceeds undisturbed therefore only in very weakly alkaline solutions, and any of a number of conditions previously unrecognized sufficed to cause the predominance of the secondary processes.

In the investigation of the mechanism of the oxidation process, many indications pointed to the fact that water was decomposed at the anode. The oxidation potential was between  $-0.70$  and  $-0.90$  volts, and below the commonly accepted anodic decomposition potential of water. Notwithstanding this it seemed probable that oxygen or some combination of it, with hydrogen was liberated at the anode by the discharge of the hydroxyl or bivalent oxygen ion. In proving this theory the author made recourse to the action of negative catalyzers, such as are designated as poisons. It was natural to suppose that if oxygen or some active oxidizing substance was liberated on the anode the finely divided platinum black of the electrode surface would act catalytically on the process by which it oxidized the  $\text{S}_2\text{O}_3$  ion. Now it is firmly established that poisons, i. e., substances which have a poisonous effect on the human system, also exert an inhibitory influence on reactions in which platinum black acts catalytically.<sup>2</sup>

If, therefore, oxygen was liberated on the anode as the primary electrode process, and if the platinized electrode surface acted catalytically on the secondary, purely chemical reaction, whereby the  $\text{S}_2\text{O}_3$  ion was oxidized, the addition of small amounts of "poisons" would retard this reaction, and should effect the potential of thiosulphate solutions, and the polarization of the anode in their electrolysis.

Numerous and diverse experiments showed that this ac-

tually occurred. The poison mostly used was mercuric cyanide, selected because it was practically non-dissociated, and of great inhibitory power.<sup>3</sup> In Fig. 1 the effect of very small quantities of  $\text{Hg}(\text{CN})_2$  on the polarization of the anode in the process  $\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-}$  is clearly shown. For the details of this and later-to-be-mentioned experiment the reader is referred to the original article in the *Zeit. f. Phys. Chem.* It

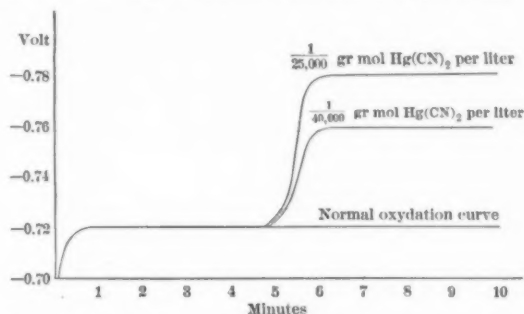


FIG. 1.—EFFECT OF MERCURIC CYANIDE ON OXIDATION POTENTIAL OF  $\text{Na}_2\text{S}_2\text{O}_3$  SOLUTION.

suffices to state here that the polarization of a platinized platinum anode on which  $\text{S}_2\text{O}_3$  ion was being oxidized to  $\text{S}_4\text{O}_6$  ion increased 0.04 volt almost instantaneously on the addition of a drop of  $\text{Hg}(\text{CN})_2$  of sufficient strength to make its concentration about one grammolecule in 40,000 liters of  $\text{Na}_2\text{S}_2\text{O}_3$  solution. A second experiment in which the  $\text{Hg}(\text{CN})_2$  was added in the proportion of 1 grammolecule in 25,000 liters, caused an increase of about 0.06 volt in the e. m. f. of polarization. Without these additions the anode polarization remained nearly constant for several hours of continued electrolysis.

That  $\text{Hg}(\text{CN})_2$  really does effect the rate of oxidation of  $\text{Na}_2\text{S}_2\text{O}_3$  solutions by oxygen gas on platinized platinum is

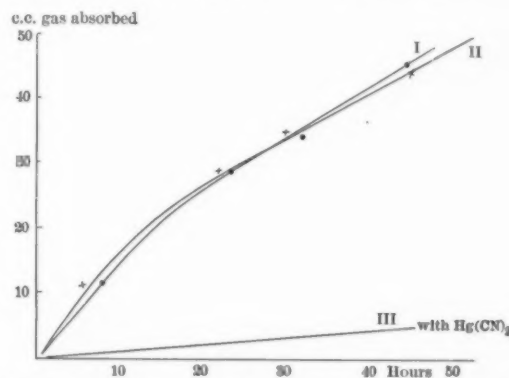


FIG. 2.—EFFECT OF MERCURIC CYANIDE ON OXIDATION OF  $\text{Na}_2\text{S}_2\text{O}_3$  SOLUTION BY OXYGEN.

shown graphically in Fig. 2. Curves I. and II. give the number of c. c. of oxygen gas absorbed per unit of time by dilute  $\text{Na}_2\text{S}_2\text{O}_3$  solutions containing a piece of platinized platinum, in two confirmatory experiments. Curve III. shows that on the addition of a very small amount of  $\text{Hg}(\text{CN})_2$  the velocity of the oxidation was greatly retarded. Other experiments, not illustrated, established the fact that the velocity of the oxidation of  $\text{S}_2\text{O}_3$  ion by oxygen gas was extremely slow without platinum.

These facts make it certain, therefore, that in the electrolytic oxidation of thiosulphates oxygen or some other active oxidizing substance (e. g., possibly  $\text{H}_2\text{O}_2$ ) is formed primarily at the anode. This theory is still further supported by the pronounced effect of  $\text{Hg}(\text{CN})_2$  and other

<sup>1</sup> *Zeit. f. phys. Chem.*, vol. 47, page 641.

<sup>2</sup> See Bredig & Ikeda, *Zeit. f. phys. Chem.*, vol. 37, page 1, and others.

<sup>3</sup> Bredig & Ikeda, loc. cit., page 58.



"poisons" on the potential of  $\text{Na}_2\text{S}_2\text{O}_3 - \text{Na}_2\text{S}_4\text{O}_6$  solutions, and by other observed phenomena. It was thus established that this oxidation is not a primary, purely electrolytic process according to the equation,



where F means the positive electric charge of a univalent gramion, but rather that it is secondary, and that the mechanism of the reaction is somewhat like



The author was able in this way to demonstrate convincingly that the surface of electrodes may act catalytically in electrolyses, and to point out, to a great degree of certitude, the probable mechanism of a complicated electrode process. We thus have an example of the value of catalytic agents in the analysis of electrode processes.

The practical bearing of this subject and the advantage of a similar intimate understanding of the mechanism of the electrode process in the development of commercial electrolytic processes may be illustrated by analogy. Here, in the case of  $\text{Na}_2\text{S}_2\text{O}_3$  oxidation was an extremely sensitive electrolytic process, one which was practically uncontrollable until its mechanism was understood, at least to some degree. But this having been accomplished, it followed logically, for reasons which it will be impossible to give briefly here, that in

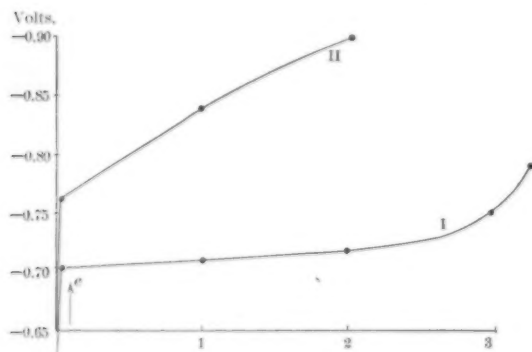
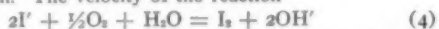


FIG. 3.—EFFECT OF IODINE ION ON POTENTIAL OF  $\text{Na}_2\text{S}_2\text{O}_3$  OXIDATION. (THE ABSCISSÆ REPRESENT HOURS.)

order to exclude the undesirable secondary reactions, and to obtain a nearly theoretical yield of  $\text{Na}_2\text{S}_4\text{O}_6$  it would be necessary to keep the concentration of the oxygen gas in the electrode as low as possible. One way to accomplish this was to accelerate reaction (3) above. This was accomplished handily by the addition of small amounts of potassium iodide to the solution. The velocity of the reaction



in the presence of platinum black is much greater than the similar oxidation of the  $\text{S}_2\text{O}_3^{2-}$  ion. The velocity of the reaction



is very great also. In the presence of iodides, oxygen, when formed at the anode, cannot attain any great concentration, therefore, before iodine is liberated and the slight amount of previously discharged  $\text{OH}^-$  ion is replaced according to reaction (4).

But the iodine oxidizes  $\text{S}_2\text{O}_3^{2-}$  ion to  $\text{S}_4\text{O}_6^{2-}$  ion almost instantaneously reforming two iodine ions (reaction (5)). The combined effect of these reactions is that after the passage of the current the  $\text{S}_2\text{O}_3^{2-}$  is oxidized to  $\text{S}_4\text{O}_6^{2-}$ , while the  $\text{OH}^-$  and  $\text{I}^-$  concentrations are unchanged.

The effect of one grammolecule of KI per 1600 liters on the oxidation potential of  $\frac{n}{10} \text{Na}_2\text{S}_2\text{O}_3$  solution is shown in Fig. 3, Curve I. The oxidation began at about  $-0.70$  volt, and increased very slowly, until the oxidation of  $\text{S}_2\text{O}_3^{2-}$  was nearly

complete. The yield of tetrathionate was about 98½ per cent of the theoretical, and no acid or sulphate was formed. Under the same conditions without the use of KI the oxidation began at about  $-0.76$  volt and increased very rapidly, as shown in Curve II. The solution quickly became acid, and much sulphur was precipitated and sulphate formed. Small amounts of iodides therefore enable us to prepare  $\text{Na}_2\text{S}_4\text{O}_6$  synthetically in solution by the electrolytic oxidation of  $\text{Na}_2\text{S}_2\text{O}_3$ , although this process otherwise is extraordinarily difficult to control. We have here an example of the value of catalytic agents in electrolytic synthetic work.

It may be argued that this is not a true catalytic action, because the manner in which the iodine ion works can be explained. On the other hand, it is catalytic in the sense that the actual concentration of the iodine ion is not appreciably changed at any time during the process, and superficially viewed it appears merely by its presence to accelerate a reaction which can occur, otherwise, of itself. In this sense it corresponds to the commonly accepted definition of a catalyzer.

A number of other pronounced and previously unknown catalytic and electrode effects were discovered which cannot be dwelt on now. They are operative, not only in the oxidation of the  $\text{S}_2\text{O}_3^{2-}$  ion, but in many other electrode processes. In this connection may be mentioned the work of Luther and Brislee on the electrolysis of chloride solutions. Subsequent to the author's discovery and proof of the secondary nature of the  $\text{S}_2\text{O}_3^{2-}$  ion oxidation, they found that the chloride electrolysis was also secondary, which they were able to prove in part by use of  $\text{Hg}(\text{CN})_2$ .

To sum up, there has been illustrated here: First, the use of catalytic agents in analyzing electrode process; secondly, by analogy, the practical use to which such agents may be put in synthetic electrolyses. It has also been pointed out that the electrode metal or substance may also act catalytically, as well as dissolved substances or the ions of dissociated electrolytes, which Prof. Ostwald has mentioned. Similar catalytic effects due to electrode surfaces or to impurities of the solution are present quite generally in electrolyses. They are not confined to the oxidation of anions, but are operative also in the reduction of anions on cathodes, either of platinum, or of the baser metals, as the author has lately found. They may be expected to extend also to the electrolytic deposition of metals, as Prof. Ostwald has pointed out. It is certain, therefore, that careful investigation and control of electrode processes with regard to catalytic influences will be of much service in increasing current yield in commercial electrolyses, and in developing and making of economic value many that are not now practicable.

## Correspondence.

### REFRACTORY MATERIALS.

TO THE EDITOR OF ELECTROCHEMICAL INDUSTRY:

Sir—Since you kindly allowed me, during my recent stay in New York, to read over the proofs of Mr. FitzGerald's article on refractory materials in electrical resistance furnaces, I like to make the follow remarks with respect to this subject. I am specially interested in it, because, about two years ago I conducted some original experiments in Maroker, Norway, with a view to getting a new highly refractory material. The furnaces were of the Siemens & Halske type, built for the manufacture of carbide of calcium on the intermittent system, and they were supplied by current from two 900-kw. three-phase generators, driven by a water turbine. The material on which I worked was native magnesite brought from Southern India. This material is found in its native condition in a

\* Luther & Brislee, Zeit. f. phys. Chem., vol. 45, page 230.

very pure state, and it has been used for generations by the natives for plastering walls of their houses and also as a refractory material.

As you are aware, a good deal of it has been mined in Southern Europe and made into bricks by being shrunk in the rotary kiln. The heat, however, from this kiln is not sufficient to wholly shrink the material or to drive off the lime and iron which is usually present. In the electric furnace I found that it was possible to pass it down the chutes in just the same way as the raw materials when making carbide of calcium, and that when once the arc was started it could be fed in at a fairly rapid rate and completely shrunk, that is to say all the  $\text{CO}_2$  being driven off without the assistance of any carbon or other material.

I made in chunks of about 15 inches cube, and after taking it out of the furnace I had considerable difficulty in breaking it with a sledge hammer. The material had a fine crystalline structure with a beautiful iridescent color, and it had evidently been in a molten condition. I made several attempts to mould the natural half-shrunk material into bricks and thoroughly treat these in the electric furnace, but with poor success.

On returning to England in November, 1902, I found my friend, Mr. Deighton, of the Hunslett Corrugated Tube Works, trying carborundum as a wash on the surface of the refractory blocks through which the water gas flame passes when heating the steel tubes. I showed him the electrically shrunk magnesite which I had made and suggested that if carborundum was good, then it was probable that this magnesite material would be even better, and considerably cheaper. As a matter of fact, it has been used as a furnace wash with considerable success. I am not able to say, of course, whether it is any better or cheaper than the siloxicon or other refractory materials which Mr. FitzGerald mentions in his most interesting article. I know of no more important subject at a moment in the electro-metallurgical practice than this question of getting a really satisfactory refractory lining. E. KILBURN SCOTT.

London, England.

#### TO THE EDITOR OF ELECTROCHEMICAL INDUSTRY:

Sir—There are a few remarks to be made on Mr. E. Kilburn Scott's letter which may be of interest.

Engels, in one of his patents (U. S. Patent 734,457, July 21, 1903) proposes to make a mixture of carborundum (crystalline silicon carbide) and a binding material, and then to apply this mixture in the wet state to fire brick, thus forming a refractory coating.

Tone refers to the use of "carborundum fire sand," one of the substances I have called "silico-carbides," as a wash on fire brick:

"A very useful mortar can be made from carborundum fire-sand by mixing with it from 30 to 50 per cent of No. 1 fire clay. \* \* \* When thinned down with water, it can be used as a wash or paint on the face of the fire brick, protecting them from the action of the fuel and the heated gases. When applied in this way to the silica lining of the Schwarz furnace, the application being made daily, or two or three times weekly, it has been found possible to obtain a life of 1000 heats without relining." (*The Foundry*, August, 1904.)

Presumably, Mr. Scott proposes to use the electrically shrunk magnesite in the same way; but I can say positively that this substance is not as refractory as the silico-carbides, or carborundum. A few days ago Mr. Bennie and I built a furnace in which we used some magnesite for part of the lining. The temperature at the inner surface of the magnesite lining was well below that of the formation of crystalline silicon carbide, but above that of the formation of the silico-carbides. The heat lasted about eight hours, and the magnesite lining, which was about 4 cm. thick, was completely fused.

It seems, therefore, probable that while Mr. E. Kilburn Scott's electrically shrunk magnesite might be most valuable

for the highest temperatures attainable in gas furnaces, it would not be of much use at temperatures which are relatively low when dealing with electrical resistance furnaces.

Unfortunately, there exists at present some confusion of terms when speaking of "high," "medium" or "low" temperatures. The use of electric furnace temperatures may practically be said to begin where combustion furnace temperatures leave off, so that a temperature which may be called "high" when referring to gas furnaces would be called "low" when working with electrical resistance furnaces.

FRANCIS A. J. FITZGERALD.

FitzGerald and Bennie Laboratories,  
Niagara Falls, New York.

#### THE EDUCATION OF AN ELECTROCHEMIST.

TO THE EDITOR OF ELECTROCHEMICAL INDUSTRY:

Sir—The letter of Mr. W. M. Sanders, which appeared in *ELECTROCHEMICAL INDUSTRY* for July apropos of Mr. Herreshoff's paper in the May issue, is interesting, stimulating and suggestive. For several reasons this subject is most germane to the question of industrial development of electrochemistry. Indeed, education considered broadly and from all points of view is the problem of the modern state; and in each branch does the future of that branch depend on the recruits called to fill up vacancies in the ranks. Happily, in chemical engineering, to-day, vacancies are caused by rapid expansion of the industry, and not by death. If the Duke of Wellington said that "the battle of Waterloo was won on the playgrounds of Eton," so too, it may be said that the metallurgical triumphs of the future are being won in the laboratories of our colleges and technical schools.

Another ground for discussing the question of the training of a chemical engineer in this journal, is that in the observation of the writer, the electrochemist should be first a chemical engineer and should hold his electrochemical knowledge as a reserve force. In the domain of metallurgy, the electro-metallurgist is doubly valuable, if his electrical knowledge is supplemented by an understanding of the capabilities of coal fired furnace, etc.

The reason for this is found in the fact that every electrochemical process (and also every electrometallurgical process) is dovetailed into a process that makes use of old reactions. Besides any electrical process uses largely the engineering practice of the profession that dates from the time when electricity started with the frictional machine and stopped with the voltaic cell. Accordingly, the apparatus and expedients of the older profession are valuable to-day in applying the new agent.

As it is necessary for the electrochemist to unite two professions, his education should be broad and liberal. The four years of a college or technical school should be supplemented by two or three years of graduate work even at a pecuniary sacrifice. Repeating the line of argument given generally in the preceding paragraph, the electrochemist should have a training to fit him for the various duties he will be called upon to fill. He should first have a knowledge of the experimental data and the principles of physical chemistry in general, and electrochemistry in particular. Secondly, he should have a knowledge of the present status of chemical and metallurgical engineering. Thirdly, he should have a trained mind, keen to grasp the essence of the problem, to analyze it, and to form his analysis to synthesize a successful course of action.

This last should be the goal of any system of education. Naturally, it is hard to attain. A legal training would be invaluable for this purpose. But a proper pedagogy would effect this result and at the same time give details of knowledge that would not be a useless appendage later. This ability is most manifest in the trained legal mind. Consider, for instance, the decision of Judge Buffington, of Pittsburg, in the

case of the Carnegie Steel Co. vs. the Cambria Steel Co., litigating as to the Jones "Mixer." It is probable that before the trial the Judge knew but little of essential features of the "direct" steel process. But on hearing the arguments of both sides, he brought out in his decision (lately upheld by the Supreme Court) the distinguishing points that were "novel and useful." Another instance comes to the mind of the writer, where the lawyers for one side read, studied and talked with their own experts until on the day of the trial they actually seemed to know more than the experts of either side. Such is the ability of a legally-trained mind.

This is a broad age, and it requires a broad education for it. In later life it is only too easy to fall into a rut—and only too hard to get out of a rut. General principles are difficult to grasp at first. The experience of a special case best drives home the generalization. General principles are still harder to apply. But in spite of all, no course of education should be considered that does not teach in some manner general principles and the means of apply them. Such a training will produce out of good mental raw material the finished product—a trained mind.

When the general principles of the science have been inculcated, then the specialization should be taken up. The specialized study should be such as to improve the general principles previously taught. The course of study should be, if possible, six or seven years. It is a matter of regret to many Americans that the American technical schools attempt "to force their students under glass." Or to subject the metaphor to violent change, applied science must not be fed to the "infant" on the "Mellon's Food" principle. Such a method in actual life does not produce the sturdy specimens, as does the prehistoric way of feeding.

Exactly how far the classical studies should be forced on the youth is a question for pedagogues to decide. Certainly, a mathematical mind has often a distaste for the classics. But psychology and the history of philosophy are requisites for a certain quality of mental fibre. Latin and Greek are not essential to culture, but they give by their clear-cut, concise grammar and the definite style of the classical authors a basis for expression in the more flexible English. An ability to put his ideas (if he has any) into suitable form, is not valueless to any engineer when he is called upon to report on a technical proposition. Constant training in English will perfect his style and make it the vehicle for his thoughts.

Of direct bearing on his later work is a knowledge of physical chemistry and chemical thermodynamics. The value of physical chemistry to the practical man is as marked as is the lack of knowledge on the part of most of them of its simplest principles. For instance, in the transactions of many scientific societies, the fallacy of Berthelot's principle of maximum heat as determining the direction of reaction is uncomplimentarily uncommon. The ignorance of the fact that the capacity of the system for doing external work nullifies the first factor and makes the law only a "half-truth." One would think that an 85-foot blast furnace, making five or six hundred tons of iron contrary to this law a day, would refute the mistaken notion. It should be a *large* argument against it.

In the study of physical chemistry, systematic experimenting will teach not only the laws, but expose the facts on which these laws are based. Thus, the embryonic electrochemist should have a course in physico-chemical measurements. This has a definite application to large-scale work. For instance, in roasting a sulphide ore, the velocity of roasting should be proportional to the cube of the oxygen-pressure on the surface of each particle of ore. So direct are the tenets of the science on practical operation of plants.

Next, this knowledge of theory and experimentation should be applied to some technical proposition. For instance, the researches of Prof. Howe and Mr. Bradford on the Ziervogel process gave as a result of a short research (but a research

most brilliantly conceived and most exactly executed) such a knowledge of the temperature limits of the reactions as to enable a metallurgist to operate the process without skilled labor. The process had been brought to the present efficient stage (as at the Argo smelter of Denver) by many years of labor and patent endeavor, by the "hit-miss-and-try-again" method.

Cheops built his pyramid by the labor of millions of men-days with wooden levers, cribbing and ropes. The Panama Canal will be built by steam shovels, dredges and modern machinery. The results are equally great, but the method of this century is relentlessly efficient and short. The comparison can be carried to the process as worked out by the Geheimrath von Ziervogel in 1840 odd, and developed in 1902 in the laboratory of the Columbia School of Mines.

Besides this training on the broad lines, some purely technical training is necessary. The electrochemist must understand something of electrical engineering and of mechanical engineering. If he is to enter the chemical side he should know something of the chemical industry; if he is to take up the metallurgical side he should be trained in metallurgy. He must know the calculus. He must know mineralogy. He must know geology. But his knowledge can be somewhat superficial in those lines (in fact, from the nature of the human mind, it must be) and provided he knows physical chemistry with an active, critical mind, he will have more than an equal chance to succeed. Needless to say, he should read the technical journals, such as the *ELECTROCHEMICAL INDUSTRY*.

After the electrochemist has had his training broad and specialized along the lines indicated above, he may enter as a freshman into the world—the university of hard work. Here he is just as green a freshman as he was when he entered the university years ago. He has his enthusiasm and energy. The older men have on the average lost those youthful traits. They have the experience. The rare example who retains his enthusiasm with the years is of the stamp of "young-old men" so happily termed by Prof. W. James. The young man is judged by his results, sometimes wrongly, but generally the world judges right.

He can do no better than follow the advice of a famous German technical professor—"See all the factories you can." It might be well to work at one plant for a year or so and then change. In the interregnum he should see at least a hundred million dollars worth of plants. He will learn in his talks with superintendents, with foremen, with workmen who talk broken English. He will see things tried by older and wiser heads than his, with looked-for success sometimes, and again with unlooked-for subsequent failure. He will learn the practical side, construction of vats, pumping and filtering corrosive liquids, leaching solids, absorbing gases, furnace design, combustion of coal and gas, conduction of heat through a charge, the heating character of a flame, handling materials and handling men. In short, he will absorb the thousand and one things that make up the practical engineer.

He will learn at work, and when he is not apparently thinking. He will find that a knowledge of the theory of choice and chance do not always conduce to a great poker player. He will see the personal equation solved before his eyes. He will learn a little by the successes of others. He will learn a little more by their failures. He will learn still more by his own successes, but most of all by his failures. He will find out that there are few things in his college course, from the athletic field to the lecture room, that did not help him, and as the writer sees things and knows things, he should not blame the broad training he has received if he does not "win out" at the end.

ELECTROMETALLURGIST.

During the eight months of the current year, ending with August, the gold production of Australia was 2,441,737 ounces. The corresponding figure for 1903 was 2,489,820 ounces.



## SYNOPSIS OF ARTICLES IN OTHER JOURNALS

*A Summary of Articles on Electrochemistry and Allied Subjects Appearing in American and Foreign Periodicals.*

### INDUSTRIAL ELECTROCHEMISTRY AND ELECTROMETALLURGY.

**Electrometallurgy of Zinc.**—In our September issue we gave some notes on recent developments in the electrometallurgy of zinc. In the *Zeit. f. Elektrochemie*, September 2 and 23, J. HESS gives a review of processes patented or described during recent years. He first deals with the electrolysis of aqueous zinc solutions and notices briefly the processes of Amberg, Strzoda, Sadtler, Ellershausen and Western, Tossizza and deals at greater length with Hoepfner's process (*ELECTROCHEMICAL INDUSTRY*, Vol. I., pages 337, 540, 568). The author then deals with electrolysis of fused zinc salts and describes the process of Swinburne and Ashcroft (*ELECTROCHEMICAL INDUSTRY*, Vol. I., page 412; Vol. II., page 404). He then gives an interesting discussion of electric furnace pro-

cesses for zinc production. The low utilization of the heat in the ordinary metallurgical zinc process is the reason why better results may perhaps be expected from the electric furnace, on account of the greater local concentration of heat in it. According to statistics of the mines of upper Silesia in 1901, there were required for 100 kg. of zinc 230 to 330 kg. of reducing material, 800 to 1100 kg. of carbon for heating, 50 to 80 kg. of clay, and \$1.07 to \$2.00 wages. Fifty to 70 per cent of the ores was calamine, the balance roasted blende. The total loss of zinc is 20 to 25 per cent. In Rheinland 300 to 400 kg. of carbon for heating are used per 100 kg. of zinc and the loss of zinc is 10 to 12 per cent with skilled workmen. The zinc ores used contain 40 to 60 per cent of zinc. One kw.-hour is equivalent to 870 kg. calories, or about  $\frac{1}{8}$  kg. of coal of 7000 kg.-calories; with a price of coal of 0.3 cent per kg., and a price of 0.3 cent per kw.-hour, one kw.-hour is equivalent to one kg. of coal. "If, therefore, the 3 to 10 kg. of coal required at present per kg. of zinc are to be replaced by electric heating, this can be done if 3 to 10 kw.-hours (according to the content of zinc in the ore) are sufficient for the production of one kg. of zinc. It is stated that in practice only about 5 kw.-hours are required for 40 per cent

ore, which would be equivalent to a seven times better utilization of heat, compared with the ordinary metallurgical process." He concludes that the electric furnace is perfectly suitable for zinc production if a larger water power is available near the zinc works. The electric furnace process is thought to be especially suitable if the zinc ores contain lead. Siemens & Halske patented the electric furnace shown in Fig. 1 (English patent 11,438, 1898). Upon the carbon tube K the condensation chamber H is set, which is surrounded by the charge, so that by heat conduction the temperature in it is maintained at 500 to 900° C., as required for condensing the vapors. The maximum temperature is at B. The slag is removed through O. The vapors escape through the carbon tube, and were expected to condense in the condensation chambers to liquid metal, but only zinc powder was obtained. C. Casoretti and F. Bertani (German patent 129,889, December 13, 1899) treat roasted zinc ores in such a way that the ore mixed with reducing agents is first heated in muffles up to the temperature of distillation of Zn, and the further increase of heat is obtained electrically. Their apparatus is shown in Figs. 2 and 3. The ore mixed with the reducing material is introduced into muffle a and drops into the muffle b,

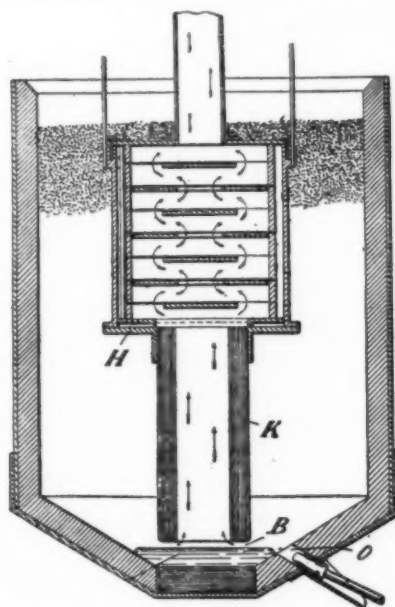


FIG. 1.—SIEMENS & HALSKE ZINC FURNACE.

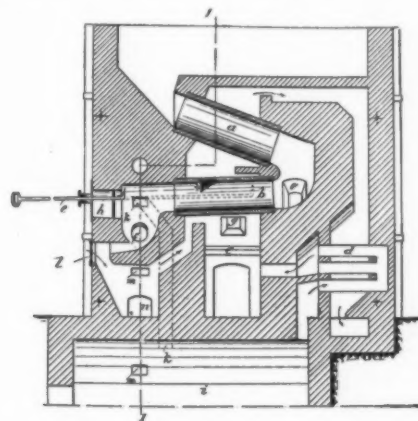


FIG. 2.—CASORETTI AND BERTANI ZINC FURNACE.

cesses for zinc production. The low utilization of the heat in the ordinary metallurgical zinc process is the reason why better results may perhaps be expected from the electric furnace, on account of the greater local concentration of heat in it. According to statistics of the mines of upper Silesia in 1901, there were required for 100 kg. of zinc 230 to 330 kg. of reducing material, 800 to 1100 kg. of carbon for heating, 50 to 80 kg. of clay, and \$1.07 to \$2.00 wages. Fifty to 70 per cent of the ores was calamine, the balance roasted blende. The total loss of zinc is 20 to 25 per cent. In Rheinland 300 to 400 kg. of carbon for heating are used per 100 kg. of zinc and the loss of zinc is 10 to 12 per cent with skilled workmen. The zinc ores used contain 40 to 60 per cent of zinc. One kw.-hour is equivalent to 870 kg. calories, or about  $\frac{1}{8}$  kg. of coal of 7000 kg.-calories; with a price of coal of 0.3 cent per kg., and a price of 0.3 cent per kw.-hour, one kw.-hour is equivalent to one kg. of coal. "If, therefore, the 3 to 10 kg. of coal required at present per kg. of zinc are to be replaced by electric heating, this can be done if 3 to 10 kw.-hours (according to the content of zinc in the ore) are sufficient for the production of one kg. of zinc. It is stated that in practice only about 5 kw.-hours are required for 40 per cent

stirring being provided by e. The muffles a and b are heated from c. In b the ore is reduced. It is then brought between the electrodes f, where it is melted with resulting total distillation. The zinc vapor passes through the canals k into the condensation room i and the slag is removed through n. It is stated that a furnace of this kind has been installed by the Societa Elettrometallurgica Lombarda, requiring per kg. of Zn two hp.-hours and 15 per cent of carbon for reduction. Experiments made to reduce zinc from unroasted blende by adding lime and carbon in ordinary furnaces have been unsuccessful. Darmstaedter (German patent 132,205, September 19, 1899) heats zinc blende in the electric furnace with additions of iron or iron oxide and carbon, whereby, instead of iron oxide, other materials like lime may be used. Zinc is distilled while calcium sulphide is obtained as fused slag. If blende is heated without addition of carbon, but with the other above additions, zinc oxide is obtained which is then treated afterwards, after removing the slag. The author describes the processes of Dorsemagen and Borchers (*ELECTROCHEMICAL INDUSTRY*, Vol. I., pages 105 and 189) and briefly mentions the processes of A. K. Picard (*Chemiker Zeit.* 46, June 10, 1903; 27, April 2, 1904), P. Danckwardt

(U. S. patent 746,798, October 15, 1903), O. W. Brown and W. F. Oersterle (U. S. Patent 742,830, May 14, 1903) and then describes the process of De Laval (*ELECTROCHEMICAL INDUSTRY*, Vol. II., October, 1904, page 423). It is stated that by this process zinc is produced with 2400 hp. in Hafs-lund, Norway. However, no ore is reduced, but only spelter is treated electrically and refined zinc of 99.9 per cent purity is obtained. A. Salgues used in Crampagna a tightly-closed electric furnace for production of zinc from ores (French patent 330,665, March 28, 1903); he gets, however, only zinc powder. The reason is that the zinc vapors are diluted by CO. In order to get solid zinc it is necessary to reduce the ores preliminarily at a lower temperature in an auxiliary furnace, so that no great quantities of CO are obtained in the distillation furnace.

**Aluminium.**—A pamphlet, issued by the U. S. Geological Survey, deals with the production of aluminium and bauxite

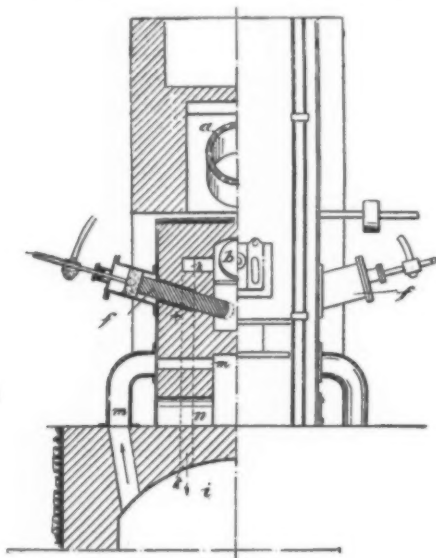


FIG. 3.—CASORETTI AND BERTANI ZINC FURNACE.

in 1903, the author being J. STRUTHERS. The production of aluminium in the United States during 1903 is estimated at 7,500,000 pounds (against 7,300,000 in 1902, 4,000,000 in 1897, 1,300,000 in 1896, 61,281 in 1890, and 83 in 1883). A review is given of the outcome of the patent litigation between the Pittsburgh Reduction Co. and the Electric Smelting & Aluminum Co. (see our Vol. I., pages 519, 522, 560). The prices of aluminium in the United States from 1901 to 1903 are given as follows:

	Small Lots	100 Lb. Lots.	1000 Lb. Lots.	5000 Lb. Lots.
No. 1 aluminium (99.75 per cent.).....	c.	c.	c.	c.
No. 2 aluminium (99 per cent.).....	37	35	34	33
Nickel-aluminium casting metal (10 p. c. ni.)	34	33	32	31
Special casting alloy (80 per cent al.).....	39	35	34	33
	35	30	29	27

The price of ingot aluminium during 1903 was adjusted by an agreement between all of the aluminium producers of the world. Then follow data on aluminium imports into the United States from 1870 to 1903. In 1903 the imports amounted to 498,655 pounds (\$139,298) of crude aluminium and 4276 pounds (\$2,818) of plates, sheets, bars and rods. The import duty is 8 cents per pound for ingot metal, and 13 cents per sheet for manufactured metal. The information contained in the pamphlet on the process of making aluminium, as practiced in the United States, contains nothing new

to our readers. Concerning the industries in foreign countries the following notes are interesting. The works of the Société Electro-Métallurgique Française, at La Praz, Savoy, France, use 9000 amperes at from 110 to 130 volts. Two of the dynamos are of the unipolar type. Aluminium is used for conductors. The output is mainly aluminium, although ferro-alloys are also made. The works of the Compagnie des Produits Chimiques d'Alais, at Calypso, near St. Michel, Savoy, France, use 4000 amperes. "The bath of fused material is covered with a layer of charcoal, which diminishes the loss of heat by radiation. The proper alumina content of the bath is maintained by spreading a fresh layer of the material on the top of the charcoal, and from time to time pushing small quantities of it into the molten bath. The condition of the electrolyte in each furnace is continuously indicated by the brightness of a 10-volt incandescent lamp. The molten aluminium, containing from 99.5 to 99.6 per cent of metal, is removed from the bottom of the bath every hour by tilting the furnace, which is supported on trunnions for this purpose." The Aluminium-Industrie-Aktien Gesellschaft has now a total of 24,000 hp. available at its three plants at Neuhausen, Gastein, and Rheinfelden; "the chief product is aluminium, but high-grade carbide is also made, and experimental work is now being carried on in other electrolytic and electric furnace processes." The works of the British Aluminium Co. have also been enlarged.

Concerning the uses of aluminium, it is said that its employment for electrical conductors instead of copper is still expanding and is one of the most important outlets for the domestic production. "A company has been formed to manufacture on a commercial scale the new explosive, ammonal, which is composed of powdered aluminium and ammonium nitrate, in respective proportions, depending upon the explosive strength desired. Ammonal is reported to be extremely safe to handle, impervious to water, and of great explosive strength." Concerning aluminium alloys, reference is made to the paper of J. W. Richards, abstracted in our Vol. I., page 498. As one of the most promising fields for the consumption of aluminium, the Goldschmidt thermit process is mentioned. A large proportion of the output of aluminium is manufactured into articles for domestic and culinary use; for construction of machine parts which require lightness rather than great strength; as a substitute for stone and zinc lithographic work; in the rubber industry for making lasts and boot trees upon which rubber shoes and boots are made; in cast-iron foundry practice as a substitute for wood in making bobbins for spinning and weaving machines treating silk fiber, and in powdered form for the manufacture of white metallic paints, a use to which it is particularly suited, on account of its non-susceptibility to atmospheric influences. Among the proposed new uses of aluminium is its substitution for the glass carboys or earthenware vessels employed for the transportation of nitric acid, and also as a substitute for zinc in lining cisterns and other receptacles for storing water.

**Bauxite.**—The same Geological Survey pamphlet of J. STRUTHERS contains the following information on bauxite. There was a large increase in the production of bauxite in the United States during the year 1903, due mainly to the development of the industry in Arkansas, the total quantity shipped amounting to 48,087 long tons, valued at \$171,306, as compared with 29,222 long tons, valued at \$128,206, in 1902. These figures show an increase in quantity of 18,865 tons, or about 65 per cent, and in value of \$43,100, or 34 per cent. At the present time, Georgia, Alabama and Arkansas, in the order of their outputs, furnish the total supply of bauxite in the United States. The world's production of bauxite in 1902 was 135,877 metric tons. The chief factor of interest during 1903 was the completion and the putting into operation of the mining plant of the Pittsburgh Reduction Co., at Bauxite, Ark. The plant has been carefully designed with the view of replacing hand labor by machinery, wherever possible. Mechanical

conveyors and elevators transport the crude ore from the cars through the mill and finally store the finished product in bins ready for shipment. A second point of interest to the industry is the new refining plant of the Pittsburg Reduction Co., at East St. Louis, which was put in operation during the latter part of the summer. The plant is similar in detail to the refining plant of the company at New Kensington, Pa. The crude ore, which was formerly shipped from Arkansas to New Kensington, is now refined at East St. Louis by the soda process, which removes the impurities, iron and silica. The equipment includes a bank of coke ovens for cooking Illinois coal, which, so far, have given very satisfactory results. If the bauxite is to be used for the manufacture of alum, it is merely crushed, dried and shipped in bulk in box-cars, but if for the manufacture of aluminium metal or artificial corundum, which requires a low silicon content, the crushed ore is first passed through a log washer in order to remove the sterile siliceous gangue. The principal salts of aluminium are aluminium sulphate and crystallized alum, for the manufacture of which bauxite and Greenland cryolite are consumed. In 1903 the production of aluminium sulphate was 80,726 short tons, valued at \$1,614,520, as compared with 80,075 short tons, valued at \$1,938,671, in 1902, and that of crystallized alum was 7574 short tons, valued at \$210,910, as compared with 8539 short tons, valued at \$299,500, in 1902.

**Electrolytic Iron.**—In view of the recent paper of Burgess and Hambuechen (*ELECTROCHEMICAL INDUSTRY*, Vol. II., page 283) an article by A. SKRABAL, published in *Zeit. f. Elektrochemie*, September 23, is interesting. He distinguishes two essential different methods yielding two different kinds of electrolytic iron. In the first method a ferrous salt is used as electrolyte, and iron as anode, with a low voltage and a low current density. He calls iron produced by this method A-iron. The second method is characterized by the use of platinum as anode, high voltage, high current density, and an electrolyte containing bivalent iron in some complex form. Iron made by this method is called by him B-iron. The A-iron is of silver-white color, compact and extremely hard. The B-iron is of more grayish color, less compact and less hard. Since the conditions of these two methods may be combined at will—for instance, ferrous chloride as electrolyte, iron as anode, high-current density and voltage, or complex ferrous salt as electrolyte, iron as anode and low current density—it is possible to get a great many different kinds of electrolytic iron which in their properties are more or less similar to A- or B-iron. The author gives some historical data on experiments made by various investigators. All make A-iron by using an electrolyte of ferrous chloride, ferrous sulphate or ferrous ammonium sulphate, perhaps with an addition of  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ ,  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{Cl}$  to increase the conductivity, while iron is used as anode. The differences in the various processes consist in the current density and temperature, while in some cases stirring is used, but not in all cases. The author describes first his method for producing a pure ferrous ammonium sulphate (Mohr's double salt). As anode he then uses a platinum electrode of 5 x 2.5 cm. size, covered with electrolytic iron by Classen's method. As cathodes he uses two platinum sheets of the dimensions 2.5 x 1 cm., which, before they are suspended in the bath, are heated to white heat and afterwards moistened with alcohol. The electrodes are suspended in the electrolyte in such a way that the distance of the upper rim from the surface of the latter is 0.5 cm.; the distance of the two cathode sheets from the anode is 1 cm. The covered beaker which contains the electrolyte must be quite high, so that the anode slime falls to the bottom without spoiling the solution. After electrolysis is completed, the cathodes are washed with water, alcohol and ether. If the anode is replaced from time to time by a new one, it is possible to obtain the A-iron in form of plates of any thickness. This iron is of a beautiful silver-white color, very bright and probably of crystalline structure. If a platinum electrode cov-

ered with such A-iron is placed in warm dilute sulphuric acid, the iron dissolves only very slowly, gas bubbles being developed on the platinum wire. Neuburger (*ELECTROCHEMICAL INDUSTRY*, Vol. II., page 319) produced electrolytic iron which did not rust. The present author did not observe this property with his iron. When exposed to moist air, it rusts, although not as easily as commercial iron. On the other hand, he obtained in some cases an iron which had an extremely high resistivity against chemical influences. The very great hardness of all A-iron is generally supposed to be due to the content of hydrogen. But the author does not think that the different content of hydrogen represents the whole difference between ordinary electrolytic iron and electrolytic iron, which has been subjected to high heat. It seems that these two represent two different allotropic conditions of iron.

**Nickel Plating.**—An article by A. A. BEADLE, in *The Metal Worker, Plumber and Steam Fitter*, and reprinted in the *Metal Industry* of September, deals with the management of nickel plating baths. Nickel platers are generally careful to procure only pure and neutral ammonium sulphate for their plating solutions, and to keep their bath permanently neutral. A comparatively soft nickel anode is better than a hard, rolled one. When an ordinary nickel plating bath, containing about  $\frac{3}{4}$  pound of nickel ammonium sulphate to the gallon of water is started, the current efficiency of the cathodic deposition is between 90 and 100 per cent. To maintain it at this value, it is necessary to maintain the nickel content in the bath constant; in other words, to see that the anode properly dissolves. The author then gives a review of the results obtained by O. W. Brown on this point (see *ELECTROCHEMICAL INDUSTRY*, Vol. I., page 487).

**Sterilizing Milk by Electricity.**—In the *Zeit. f. Elektrochemie*, of September 2, G. GUARINI gives a brief outline of experiments made on the sterilization of milk. If the milk is heated, its chemical composition is changed, and this should be avoided under all circumstances. The author, together with Samarani, used alternating current of 110 volts and carbon electrodes. At another place he speaks of platinized carbon electrodes. The current and frequency are not given, but it is stated that if the current is strong enough the milk will be completely sterilized without any coagulation. Two points are of special importance, the length of treatment and the current.

**Electrometallurgy of Iron and Steel.**—An illustrated review of the various types of electric furnace, proposed for this purpose, is given by A. F. SCHNEIDER in the August issue of the *Mining Magazine*. The article contains nothing new to our readers, except the diagrams on page 115, which, however, lack explanation.

#### THEORETICAL AND EXPERIMENTAL.

**Electrolysis of Potassium Acetate.**—A paper by F. FOERSTER and A. FIGUET, published in *Zeit. f. Elektrochemie*, September 16, deals with the anodic reaction during electrolysis of potassium acetate with anodes of different materials. The authors showed that three main phenomena are to be distinguished: First, development of oxygen; second, oxidation of acetic acid to carbonic acid; third, formation of ethane. According to the nature of the anode material one or the other of these different reactions prevails. The main point of interest is that the action of the anode metals is the same as should be expected from their anode potentials in electrolytes when developing oxygen.

**Anodic Development of Oxygen.**—In connection with the article of F. Foerster on electrolysis at smooth and platinized platinum anodes published in our Vol. I., page 443, the results given in *Zeit. f. Elektrochemie*, September 9, by F. FOERSTER and A. FIGUET should be interesting. Former authors have already pointed out that a different anodic poten-



tial is required at anodes of different materials in order to start the development of oxygen. The present authors have investigated how the anodic voltage required for continual development of oxygen during continuous electrolysis at different anodes changes with the time. Part of the results are given in Fig. 4, which refers to electrolysis of  $2\text{N KOH}$  with one ampere, with a current density of 0.033 ampere per square centimeter at  $15^\circ \text{C}$ . It will be seen that at polished platinum the anodic voltage increases rapidly, and, after one ampere-hour, reaches a constant value. Iridium shows the peculiar feature that the voltage having reached a maximum is then decreasing again; this is due to the fact that iridium

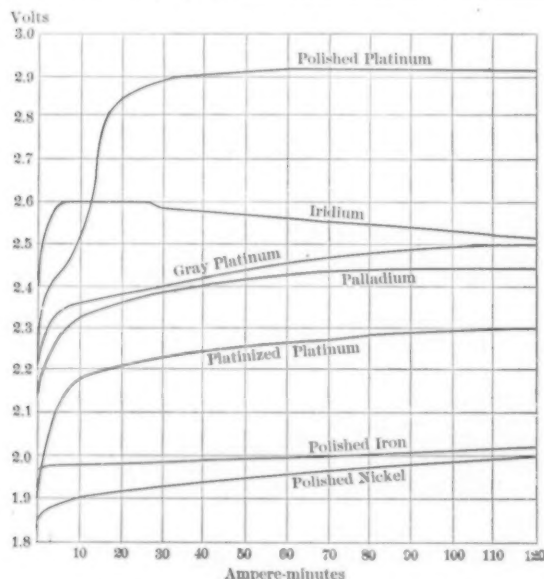
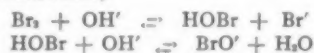


FIG. 4.—POTENTIAL REQUIRED FOR OXYGEN DEVELOPMENT.

dissolves in small quantities. The author gives his reasons why he believes F. Haber's explanation to be correct that polished electrodes at which gas is developed are surrounded during electrolysis with a thin atmosphere of gas, which is kept attached to them by adsorption.

**Electrolysis of Bromides of Alkalies.**—While the phenomena during the electrolysis of chlorides and iodides have been carefully analyzed during recent years, the analogous phenomena during bromide electrolysis have been less studied. H. KRETZSCHMAR, in a long paper published in *Zeit. f. Elektrochemie*, October 7, gives an account of an experimental investigation which enables us now to compare completely the electrolysis of chlorides, iodides and bromides. The author first studied the purely chemical side of the question, i. e., the action of bromine upon alkalies. When bromine acts upon an alkali hydroxide solution, always hypobromite is first formed. The process proceeds in such a way that the following two equilibria result,



When one molecule of bromine acts upon an equivalent of alkali, considerable quantities of both remain first unchanged. Hypobromous acid and bromide act upon each other even at very low concentration and yield free bromine and alkali, or hypobromite. Whenever hypobromous acid, or bromine, come into contact with hypobromite, bromate is formed according to the equation,



This process is quite analogous to the formation of chlorate from hypochlorous acid, or free chlorine, but there are the

following differences. The formation of bromate has a velocity constant 100 times that of chlorate formation; and, on account of considerable hydrolysis of hypobromite, the bromate formation starts even in a slightly alkaline solution with considerable speed. In a somewhat more alkaline solution (0.1 normal or more) hypobromite and hypochlorite are stable to about the same degree. With increasing alkalinity the speed of the hypobromite solution increases again slowly. A second process sets in, which leads from hypobromite to bromate, but has a very much lower speed than the first one.

Concerning the electrolysis of bromide solutions, Kretzschmar has established the following facts. When neutral bromide solutions are electrolyzed, free bromine is developed at the anode. The bromine, reacting with the free alkali coming from the cathode, yields hypobromite. The concentration of hypobromite reaches a constant value, when the electrolysis is continued for some time; only bromate is then formed in the solution, which before that moment increased more slowly than the hypobromite. At a polished platinum anode oxygen is developed in increasing quantity with increasing content of hypobromite in the solution; the proportion of the current which produces oxygen, becomes constant with the hypobromite concentration and is never more than 9 per cent of the total current. At a platinized anode the anodic development of oxygen is very small, with moderate stirring and the current which produces oxygen is less than 1 per cent of the total current. In other words, the efficiency of the formation of the bromine-oxygen compounds is almost theoretical. At the same time, the anode potential is only about 0.3 volt less negative than at a polished anode under otherwise the same conditions. The hypobromite concentration which can be obtained is the higher, the higher the bromide concentration and the current density and the lower the temperature; it is higher at a platinized anode than at a polished anode. During electrolysis of strongly alkaline bromide solutions, hypobromite is again first formed up to a concentration, but at the same time bromate is formed from the beginning in considerable quantities. Even in normal alkaline bromide solution free bromine may be obtained at the anode in visible quantities; and this takes place more easily at a platinized than at a polished anode, and in greater quantities with increasing bromide concentration and current density. If free bromine is not developed in considerable quantities at the anode, only a small hypobromite concentration is obtained, and the anodic development of oxygen decreases with progressing formation of hypobromite, the proportion of the current consumed for the generation of oxygen being about 10 per cent of the total current. The author develops his theoretical views on the primary or secondary nature of the various ionic reactions. He finally gives the following table:

There is Formed	In Acid Solution	In Neutral Solution	In Strong Alkaline Solution
Chlorate..	Secondarily	By anodic discharge of $\text{Cl O}'$	
Bromate..	Secondarily		By anodic oxidation of $\text{Br O}'$
Iodate....	Secondarily		

**Electrolysis of Copper Sulphate.**—In the *Zeit. f. Elektrochemie*, September 16, F. FOERSTER and G. COFFETTI discuss the various ionic reactions at the anode and cathode during copper sulphate electrolysis. They refer to the fact that if a platinum cathode is suspended in a normal copper sulphate solution, current passes, even when its potential is still about 0.1 volt more negative than the proper potential of copper against the solution. In this case no copper is deposited upon the cathode, but the reaction consists in the cathodic re-

duction of bivalent copper to monovalent copper. While the article is mainly theoretical, the views expressed by the authors throw some light on various facts known to copper refiners. At the copper anode the following three processes may occur:

- (1)  $\text{Cu} + \text{F} \rightarrow \text{Cu}^+$
- (2)  $\text{Cu} + 2\text{F} \rightarrow \text{Cu}^{++}$
- (3)  $\text{Cu}^+ + \text{F} \rightarrow \text{Cu}^{++}$

where F means a positive charge of 96,540 coulombs (one positive electron). These three processes will go on in such a way that an equilibrium between  $\text{Cu}^{++}$  and  $\text{Cu}^+$  near the anode, is established according to  $\text{Cu}^{++} + \text{Cu} \rightleftharpoons 2\text{Cu}^+$ . As long as the solution is far from this equilibrium that one of the three reactions (1), (2), (3), will take place which is able to establish the equilibrium. Thus, if a copper anode is suspended in a copper-sulphate solution reaction (1) will take place and will produce the necessary quantity of cuprous sulphate. But if this quantity should for some reason become greater than required for the equilibrium, the reaction (3) will regulate the matter. When the equilibrium at the anode is then reached, (1), (2), (3) go on simultaneously in such a way that the equilibrium is maintained; that means, reaction (2) prevails, and with respect to the dissolved quantity of copper the total effect is the same as though reaction (2) was the only one, as long as there is no influence exerted on the  $\text{Cu}^+$  ions in the solution; but this is always the case. As well known, during electrolysis with pure copper anodes, their decrease in weight is not inconsiderably greater than the quantity of copper simultaneously deposited on the cathode. This great decrease of anode weight is sometimes assumed to be due to the action of atmospheric oxygen upon the anode copper, although this would not explain why the anodes dissolve uniformly over the whole surface, and are not attacked most strongly at the contact points of the solution and the air. As a matter of fact the action of atmospheric oxygen upon the quantity of copper dissolved from the anode is only indirect, in so far as cuprous sulphate produced by the current is oxidized to cupric sulphate by means of the reaction  $\text{Cu}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{O} \rightarrow 2\text{CuSO}_4 + \text{H}_2\text{O}$ ; in this way the concentration of cupric sulphate increases and sulphuric acid is consumed. This is the process which in copper refining has an unfavorable effect on the conductivity of the electrolyte, so that the latter must be regenerated from time to time in tanks with insoluble anodes. Increasing temperature favors the cuprous sulphate formation at the anode and at the cathode. Schwab and Baum's experiments (ELECTROCHEMICAL INDUSTRY, Vol. I, pages 484 and 584) confirm this and show the fact that the relation of anode loss to cathodic deposit approximates the value unity with increasing current density.

**Deposition of Zinc from Zinc Chloride Dissolved in Acetone.** The October issue of the *Journal of Physical Chemistry* contains a full account by H. E. PATTEN of his experimental investigation, a preliminary account of which was published in our August issue, 1903. From his later experiments he concludes that the deposition of zinc from acetone solution is not well adapted to produce chemically pure zinc or to give a thick coat for chemical purposes. This does not diminish, of course, the scientific interest of the work.

**Electrolytic Solution of Platinum in Hydrochloric Acid.**—Platinum is generally used for electrodes, in spite of its high price, on account of its resistivity against chemical reagents. In ordinary work platinum is considered practically indestructible. Nevertheless, it has long been known that under certain conditions platinum may dissolve, and it is of importance to know these conditions in order to guard against them. In *L'Electricien*, of September 10, D. TOMMAST gives some notes on the electrolytic solution of platinum anodes in hydrochloric acid solutions. He experimented with a U-tube in the two arms of which two electrodes of chemically pure platinum were suspended, the current being furnished by two Daniell

cells in series. With fairly concentrated hydrochloric acid, density 1.180, he first did not get any development of gas at the anode; at the end of an hour a few gas bubbles appeared at the anode, while after twenty hours the production of compounds, containing oxygen and chlorine, still continued at the anode. Upon analysis of the liquid a residue of perfectly pure platinum was obtained, but the quantity is not stated. With smaller concentrations of hydrochloric acid, less and less platinum dissolves, until in a solution containing 5 c. c. of acid of density 1.180 and 100 c. c. of distilled water, no trace of platinum could be found in the liquid, after the current had passed for 100 hours.

**Ionic Mobilities and Conductivity.**—F. KOHLRAUSCH's classical researches on the conductivity of dilute aqueous solutions are well known. For very dilute solutions his conductivity measurements, taken together with the determination of transport numbers by Hittorf and expressed in the terminology of the model of traveling ions, led him to the fundamental result that the conductivity is directly proportional to the sum of the ionic mobilities of the ions participating in the transportation of the current, whereby each ion has a distinct mobility depending only on its chemical nature and independent of the other ions present in the solution. He showed that when the mobilities are known, the conductivities may be calculated with a high degree of accuracy. These researches were to the greatest part confined to monovalent ions. F. KOHLRAUSCH and E. GRUENEISEN have now examined the conductivities of aqueous solutions of electrolytes with a number of bivalent ions, such as Ba, Sr, Ca, Mg, Zn, Cd, Cu, Pb in the form of sulphates, nitrates and chlorides. The results are published in the *Sitzungsberichte der Preussischen Akademie der Wissenschaften*, July 28, and an abstract is given in the *London Electrician*, September 30. The authors find considerable difficulty in deriving the conductivity from the ionic mobilities. To obtain the conductivity at infinite dilution by extrapolation is more difficult than it is in the case of monovalent ions, since the rise is from two to five times as great. The difficulty, which can be more or less surmounted when at least one of the ions is monovalent, becomes insuperable when both are bivalent. The supposition that an ion has always the same mobility at a very high dilution is conditioned by the water taking no part in the conduction. This is no doubt true at infinite dilution, but there is no knowing up to what dilution the influence of the water continues to be felt. Hydrolysis is more likely in the case of bivalent ions than in the case of monovalent ions. A fraction of 1 per cent in the way of hydrolysis would account for the discrepancies found in magnesium sulphide. It is remarkable that all recent experimental investigations in the theory of solutions point to the importance of taking the influence of the solvent into account.

**Transport Number of Sulphuric Acid.**—O. F. TOWER has made a very careful redetermination of the transport number of sulphuric acid. The results are published in the September issue of the *Journ. Am. Chem. Society*. From experiments made between 8 and 32° C., and with concentrations between normal and 1/50 normal, he finds that in dilute solutions the transport number may be represented by  $0.1788 + 0.0011(t - 20)$ , when t is the temperature in degrees Celsius. There appear to be no  $\text{HSO}_4^-$  ions beyond the concentration 1/10 normal. The most probable value of the migration number (mobility) of the  $\text{SO}_4^{--}$  ion is 70, in accordance with F. Kohlrausch.

#### MISCELLANEOUS.

**Anaconda.**—To the *Engin. and Mining Jour.* of September 22, CHARLES S. PALMER contributes an article entitled "the casual observer at Anaconda." A very concise outline is given of the plant and the process. He sums up his main impressions as follows. "The great phenomena, aside from the general magnitude of this 5000-ton plant, should include the

use of compressed air, both in furnace and surface traction, the fairly successful attempt to save and re-treat flue-dust, the saving of steam fuel by the harnessing of the reverberatories to the Sterling boilers, and the high degree of purity of the anode copper. Any one coming away from the new works cannot overlook the long string of ruins representing the old works, from the refuse of which thousands of tons of material of every description are being treated every month." The anode copper was formerly refined at the large electrolytic refinery at Anaconda; but the metal is now shipped East for further treatment. The anode copper as finished at the Washoe works, runs about 99.6 in copper, and with some gold and considerable silver, so that all the work done at Anaconda is now simply one of concentration of values.

**Wet Process for Copper Extraction.**—The mines department of Queensland had requested L. C. BALL to collect information concerning wet copper processes, especially those applicable to Queensland ores. His report is published in the *Queensland Gov. Mining Jour.* of May and June, and is a concise summary of the various processes. A long abstract of it is given in the *Mining Magazine* of September.

**Metallurgy of Copper, Lead and Zinc.**—A very interesting general outline of the development of the metallurgical methods now in use in this country for the treatment of copper, lead and zinc ores, is given by W. R. INGALLS in the July issue of the *Mining Magazine*. The author emphasizes it is the best metallurgical practice which extracts the most money from a given kind of ore. This principle should always be kept in mind. "Attention is frequently called to the waste of sulphur in burning sulphide ores. It would, indeed, be a waste if there were a market for sulphuric acid where such ores are smelted, but if there be no market it may not be a waste at all." The author deals at some length with roasting furnaces and processes, and briefly discusses the problem of pyritic smelting.

**Cadmium in Spelter.**—Some editorial remarks are made in the September issue of the *Metal Industry* with respect to the effect of cadmium, contained in certain varieties of spelter, upon brass. The writer does not share the opinion, sometimes expressed, that cadmium is harmful. He conducted a series of experiments on the influence of cadmium on the rolling properties of brass, and amounts of pure cadmium were added to brass in quantities up to 0.50 per cent without showing that it had any deleterious effect beyond a slight hardening. As far as the influence of cadmium on the casting qualities of brass is concerned, the opinion is expressed that it may have rather a good effect. Cadmium has a strong affinity for oxygen and so acts as a deoxidizer. In fact, it has become standard practice to add cadmium to sterling silver for this purpose.

**Analysis of Molybdenum in Steel.**—In the June issue of the *Jour. of the Amer. Chem. Socy.* F. VAN DYKE CRUSER and E. H. MILLER discuss the best method for accurately and rapidly estimating molybdenum in steel and steel-making alloys. The main result is that molybdenum can be completely separated from an acid solution containing iron, using hydrogen sulphide under pressure, the precipitate being slightly contaminated by iron, which is probably held mechanically and cannot be washed out; it is necessary to remove this iron subsequently by ammonium hydroxide. This method of separation of molybdenum from iron is more accurate than the use of either sodium or ammonium hydroxide.

**Determination of Sulphur in Iron.**—In a critical discussion of the usual methods for this purpose, published in the July issue of the *Jour. Amer. Chem. Socy.*, A. P. FORD and O. G. WILLEY strongly recommended Bamber's method. They use it as follows. A 2-gram sample of drillings is dissolved slowly in nitric acid in a platinum dish, using an inverted watch-glass over the drillings. After the iron is completely dissolved the watch-glass is removed from the solution, 1 gram of potassium

nitrate added and the solution evaporated to dryness and ignited over a Bunsen burner at a good red heat for three or four minutes, turning the dish so that the side, as well as the bottom is heated to redness. Add 50 c. c. of 1 per cent solution of sodium carbonate, boil for a minute or so, filter, using paper pulp, and wash with hot 1 per cent sodium carbonate. Acidify filtrate with hydrochloric acid and evaporate to dryness. Take up in 50 c. c. water and 2 c. c. strong hydrochloric acid, filter, wash, and in the filtrate, which should be about 75 or 100 c. c. in bulk, precipitate the barium sulphate with barium chloride.

**Pig Iron from Briquettes.**—One of the difficulties arising in connection with magnetic separation of iron ores is due to the difficulty of treating the fine concentrates in the blast furnace. Various means have been tried to overcome this difficulty. In a very original way, for instance, M. Ruthenburg applies the electric furnace to agglomerate the fine particles and bring them to a temperature at which they may be reduced afterwards in a soaking pit. On the other hand, many attempts have been made to briquette the concentrates, and a very interesting article concerning a process of this kind worked at Herraeng, Sweden, is described by HENRY LOUIS in the *Jour. of the Iron and Steel Institute* of May. The magnetite received from the magnetic concentrators is mixed with a binding material and stamped into briquettes which are burned in the briquetting furnace. The temperature in the latter reaches 1300° C., and at this heat the magnetite agglutinates sufficiently to form a firm, hard briquette. At the same time the briquette furnace acts as an exceptionally efficient calciner for removing practically the whole of the sulphur; the concentrates retain a notable proportion of sulphur, but this is almost entirely eliminated in the briquetting process, as shown by the following analysis of a briquette:

	Per cent.
Silica .....	7.50
Peroxide of iron .....	86.99
Protoxide of iron .....	0.55
Alumina .....	0.80
Oxide of manganese .....	0.70
Lime .....	3.40
Magnesia .....	0.20
Phosphorus .....	0.002
Sulphur .....	0.016
	100.158
Metallic iron .....	61.32

The briquettes are then hoisted to the top of a pair of charcoal blast furnaces, where they are smelted for high-class pig iron; the waste gases from the blast furnace fire the briquetting furnaces, supply gas for the engines which furnish the blast, and also drive the dynamos of an electric central station, from which power is conveyed to the concentrating works, as well as to the various mines for hoisting, pumping, etc.

**Fuel Briquetting.**—The October issue of *Mines and Minerals* contains the first of a series of articles by J. FULTON on the fuel briquetting industry. The author deals with the materials of which bricks are made, the binders, the fuel value, the shapes of briquettes and describes the processes and machinery used.

**Bricking.**—A bricking plant for flue dust and fine ores is described and illustrated by J. C. BENNETT in the *Engr. and Min. Jour.*, September 15.

**Quicksilver.**—A long article by W. FORSTNER on the quicksilver deposit of California is published in the *Engr. and Min. Jour.*, September 8 and 15.

**Gold.**—The October issue of *Mines and Minerals* contains the first part of an illustrated article by F. A. THOMSON and S. L. GOODALE on the 300-ton chlorination plant of the Portland Gold Mining Co. at Colorado Springs, Col. In the pres-



ent installment the crushing, sampling, bedding and roasting of the ore is described.

**Manufacture or Repair of Articles Made of Quartz.**—A note in the London *Electrical Review* of September 30, gives the following abstract of a German patent granted to P. ASKENASY. "A quantity of quartz sand is laid upon a suitable support of the same material, and fused into the desired shape by means of an electric arc, which is moved over the surface of the mass as it melts. When such an object as a basin is being made, the quartz is first mixed with some agglutinant, such as 1 per cent of starch solution, petroleum residue, lavender oil, or the like. The arc is struck between sloping electrodes of small diameter, high voltages being employed; and in order to hinder their rapid consumption, the operation is conducted in an indifferent atmosphere, such as one of carbon monoxide. In certain cases it may be desirable to add to the quartz some metallic oxides, like alumina, stannic acid, titanitic acid, etc., as these reduce the melting point; but the quantity introduced must be too small seriously to affect the coefficient of expansion. During the fusion a dust of quartz may be allowed to fall round the arc, for in this manner any holes produced are instantly sealed up. The same process is available for the repair of any cracks or flaws in articles already constructed of quartz."

**Evolution of Metallic Structure.**—In a paper published in *Comptes Rendus*, August 16, and abstracted in the London *Electrician*, of September 9, G. CARTAUD reports having found traces of a cellular structure in the soft metals, lead, tin and zinc, which he has succeeded in polishing and etching. Lead, which is the most difficult to polish, also presents the most

decisive evidence of cellular structure. When attacked by picric acid dissolved in acetone it shows a completely closed microscopic net work of cells. "There is, however, evidence to show that this network is shown up by a kind of development, and is but the relic of an actual structure in what might be called the embryonic stage. Apart from this small cellular network, there is a much larger crystalline network which indicates the final stage of the solidification." The lines of this network are straight, and freely intersect the waving lines of the celluloid network. The author compares them to lines drawn along the course of a river, but so as to indicate the general or embryonic lines, but rectifies them. When an ingot is deformed and then annealed the relation between the crystalline and the cellular network disappears.

**Mining in the United States.**—The *Mining Magazine* of July contains an article, with map, by F. L. Ransome, on the geographic distribution of metalliferous ores within the United States, and an article by H. S. Fleming on commercial divisions of the competitive coal makers; in the August issue J. F. Kemp writes on the formation of veins, G. H. Ashley on the Cumberland Gap coal field; in the October issue E. C. Eckel gives a statistical review of the non-metallic mineral products of the United States, U. S. Grant on the Lake Superior iron ore deposits, W. H. Weed on occurrence and distribution of copper in the United States, D. H. Stovall on placer and hydraulic mining. In the July and August issues C. Henrich gives an interesting illustrated outline of silver mining in the Guanajuato district in Mexico.

**Timbering in Mines.**—A long illustrated article by J. H. BATCHELLER on timber and timbering may be found in the *Engin. and Min. Jour.*, September 15, 22, 29.

## ANALYSIS OF CURRENT ELECTROCHEMICAL PATENTS.

BY GEORGE P. SCHOLL, PH. D.

### ELECTRIC FURNACE AND FURNACE PRODUCTS.

**Compensating Terminal for Electric Furnaces.**—H. N. Potter, New Rochelle, N. Y. Patent 770,312, September 20, 1904. Application filed August 6, 1903.

The object of the invention is to provide means for compensating the expansions of the various materials which constitute the terminals of an electric furnace, f. i., in cases where the furnace body consists of graphite, while the current terminals are of metal. Such compensation is for the purpose of preventing distortion of the terminals under the action of heat and consequent loss of energy by the increase of resistance. The drawing accompanying the specification shows such a terminal applied to a tube furnace. The tubular part of the latter fits into a terminal of the same material, also of tubular form, the second half of which is enlarged to about three times the diameter of the first half. Its outer end abuts against a terminal of copper, of still larger diameter. The graphite and the copper parts are joined by means of iron or steel bolts, which pass through the copper part, and without touching the graphite part, are connected to a flange resting upon the enlargement of the latter. It is stated that the essential thing in order to make the terminal "compensating" terminal, is that the bolts should have a co-efficient of expansion intermediate between that of the copper and the graphite terminal. Then by properly dimensioning the latter, the reactions of the parts under the influence of heat will just balance each other, so that the pressure between the two parts will practically remain constant under variations of temperature.

**Incandescent Electric Material.**—A. Voelker, Berlin, Germany. Patent 770,991, September 27, 1904. Application filed June 2, 1904.

The process of manufacturing the above incandescent material consists in the granulation of carbon until the individual grains are substantially from one to seven millimeters in size. The material thus obtained is divided into groups, the first of which contains only grains of one millimeter thickness, the second grains of two millimeters, and so on. The conductivity of the various groups is graduated as desired either by the addition of graphite or of silicates, according as to whether the conductivity is to be increased or decreased. What particular silicates are to be added, is not disclosed by the inventor, notwithstanding that it would be a very important thing to know. The new material is stated to be spread in the same manner as fuel over the surface which is to be heated, or it is heaped up around the object to be heated, f. i., a crucible, muffle or furnace chamber.

**Apparatus for Electric Heating.**—W. S. Horry, Niagara Falls, assignor to Union Carbide Company, Patent 771,249, October 4, 1904. Application filed June 28, 1904.

The furnace is intended more specifically for the production of calcium carbide by the use of a polyphase alternating current, preferably one of many phases. The body to be heated is preferably circular, and one set of the terminals of the various phases of the current is connected to equidistant points around its circumference, while the other set of terminals is connected to a common or neutral point. The fur-

nace is illustrated in cross-section in Fig. 1. It consists of an annular stack provided with charging bell and hopper and outlet pipe 12 for the waste gases. One set of dynamo terminals is connected to the electrodes 1 to 8, the number of which is the same as the number of fixed successive windings in the fixed armature of the dynamo. The electrodes are cylindrical carbon rods, and eight of them are shown in each horizontal series, but in practice a much larger number is desirable. The electrode 9, which extends through the bottom of the furnace is connected to the neutral point of the dynamo. It may be provided with a central vertical tapping hole, 13, for withdrawal of the molten product. A large number of electrodes are preferably used, inasmuch as it is then possible to employ relatively small electrodes without unduly heating them or their terminal connections. For starting the furnace it is fed with an initial charge of lime and carbon, which may be one containing large pieces of carbon, which, by being in contact with each other at various points, afford directly a path for the current. In case the charge consists of a non-

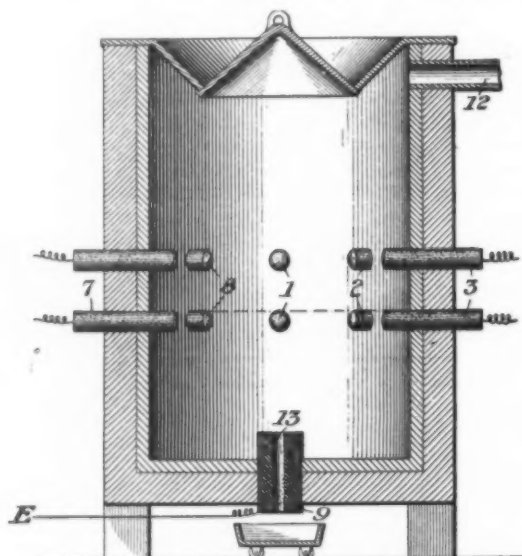


FIG. 1.—ELECTRIC FURNACE.

conducting mixture of coke and lime, an initial path for the current has to be provided by the use of a conducting charge or otherwise. In the normal working of the furnace the charge above the electrodes is heated sufficiently by conduction and radiation and by the waste gases arising from the zone of reduction. The furnace works continuously, the molten material being tapped out and fresh material charged as required. Polyphase currents used in this connection have the advantages that practically the maximum voltage of the generator is always maintained along one path through the material under treatment, the working current thus being the maximum current of the generator all the time, instead of varying from zero to a minimum. The total cross-section of the electrodes can also be smaller than for a furnace of the same capacity using single-phase current, and any electrode may be removed and replaced without interfering noticeably with the operation of the furnace. The advantages of the direct current are claimed to be retained, without the disadvantage of the electrolytic effects which always accompany its use. The source of the current may be a transformer with a number of separate windings, one end of each winding being connected to a common point, and the other one to one of the electrodes. It is claimed that the distinguishing feature of the invention is the use of a source of current having a star winding, and the provision of a neutral or com-

mon electrode in contact with the body to be heated. It is also claimed that a body of carbide forming materials or other charge may be heated to a temperature sufficient to effect the desired reaction, by employing a layer of molten iron rod or carbide of iron placed in the lower part of the furnace, and causing the various phases of the current to pass from terminals placed around and in contact with the iron to the central electrode, the iron thereby acting as a resistance conductor.

*Apparatus for Electric Heating.*—W. S. Horry, Niagara Falls, assignor to Union Carbide Company. Patent 771,250, October 4, 1904. Application filed June 28, 1904.

The furnace differs from the one described above inasmuch as it has no common terminal for the various phases of the polyphase current. Instead of that, the electrodes are distributed in one or more rows at equidistant points around the periphery of the furnace, and the terminals between which the maximum difference of potential establishes itself, are arranged at opposite ends of the diameter of the circle. The current, therefore, successively shifts between succeeding pairs of opposite terminals as the phases shift in the windings of the dynamo. As currents also flow across the furnace from each electrode to all others, the material lying within the path of the current is very uniformly heated. The furnace illustrated in the specification is stated to be intended for the production of calcium carbide, and designed to receive a current of 2000 kw. or more. It has two horizontal rows of electrodes, twenty-four in each row. A tapping hole is provided on a level with the bottom of the furnace. The production of carbide is continuous, the furnace has to be started in a manner similar to that described above.

*Furnace for the Manufacture of Steel.* Gustave Gin, Paris, France. Patent 771,872, October 11, 1904. Application filed June 30, 1903.

The furnace described in this application has already been made known to the electrochemical world through articles by Mr. Gin, in which besides describing the furnace, he gives a good deal of theoretical information and elaborate thermochemical calculations concerning the processes which might be carried out in it. A lengthy abstract was given by Mr. Bennie, in *ELECTROCHEMICAL INDUSTRY*, Vol. II., page 20. The illustrations of the construction of the furnace which accompany the present specification, are exactly the same as those given in the latter article. Briefly recapitulated, the furnace consists of a movable truck, on which is placed the refractory hearth. Winding channels are arranged within the latter for the purpose of containing the fused metal which is to be treated in the furnace, and current is led in at the ends of this liquid column by terminals made of bowl-shaped, hollow and water-cooled blocks of steel. The hearth fits into an oven-shaped structure. Practical data as to the dimensions of such a furnace in practice, or its practical operation are not given; it is only stated that the pig iron is introduced in a liquid state through funnel-shaped openings provided in the roof for that purpose. It is claimed that any of the known processes for making steel can be used, and that the pig and scrap process can be easily practiced by adding to the melted pig iron the proportion of scrap which after being dissolved in the bath will give the right amount of carbon in the finished product. To any one who has seen the heterogeneous mass of iron rubbish of all kinds, called scrap, on the charging floor of an open hearth furnace, it would appear as though the melter and his helpers would have a good deal of difficulty in distributing that scrap evenly over the long narrow channels, so as to make a uniform reliable product. It is stated that the pig and ore process can also be used, and the addition of ore is made as in any other furnace in successive portions until the carbon is practically eliminated. The above remarks apply also to this process. A small opening is provided at the front of the furnace for raking off the

slag, but as the slag will form all over the long channels, it will require a good deal of hot work on the part of the melter to get it to the front.

#### ELECTROLYTIC PRODUCTION OF METALS AND COMPOUNDS.

**Manufacture of White Lead.**—Jacques Oettli, Lausanne, Switzerland. Patent 771,024, September 27, 1904. Application filed July 6, 1903.

The process consists in the electrolysis of 1 per cent solution of common salt, which quantity must not be exceeded, since experience has proved that a more concentrated solution gives rise to other compounds. The electrodes are plates of lead, and the most suitable current density is 1 ampere per square decimeter. It must in no case exceed 2 amperes per square decimeter. A too great current density produces formation of compounds of lead resulting from the oxidation of the chloride, f. i., peroxide of lead, and through them of several oxychlorides of lead, the avoidance of which formation is important. The temperature of the electrolyte should not exceed that of the surrounding air, about 15 degrees C., as a higher temperature would probably lead to the formation of peroxides and oxychlorides of lead. The reactions taking place during electrolysis consist in the formation of chloride of lead at the anode by means of the chlorine liberated there. The chloride is transformed by the hydrate of sodium formed at the cathode into hydrate of lead, sodium chloride being reformed. The production of hydrate of lead is stated to be very rapid, and the anode is covered by a deposit, causing polarization. In order to prevent this deposit, and at the same time to use both electrodes, the current is reversed at short intervals, every five or ten minutes. Experience is stated to have shown that this method gives good results, both in regard to the quantity and the quality of the product obtained. Circulation of the liquid is necessary to keep the temperature of the electrolyte within the required limits. The hydrate of lead is carbonated by means of carbonic acid, and it is stated that the white lead is of better quality if the carbonation takes place at the moment when the hydrate is formed. It is, therefore, preferred to carbonate in the electrolytic tanks, carbonic acid being introduced into them until the basicity of the liquid begins to disappear, care being taken, however, not to neutralize the hydroxide completely. The liquid containing the white lead which settles at the bottom of the tanks is then syphoned off, the product is thoroughly washed and passed through a filter press and dried very slowly, the paste being first exposed to the open air (stretched on a large surface) and then finished in drying rooms by means of hot air, at a temperature not exceeding 50 degrees C. The theoretical voltage of decomposition of chloride of sodium is 4.2 volts, therefore, counting in the loss of resistance, 5 volts are required for every tank. The tanks are preferably of wood rendered water tight, and are preferably lined with lead. The lead electrodes are preferably cast plates on 1 cm. thickness and 1 square meter of surface. Badly refined lead, which contains iron, copper, arsenic or antimony, produces white lead of an inferior quality, contaminations of copper being especially to be avoided.

**Manufacture of Zinc White.**—Jacques Oettli, Lausanne, Switzerland. Patent 771,025, September 27, 1904. Application filed July 6, 1903.

The method depends on the electrolysis of a warm solution of sulphate of sodium, or of any other alkali salt of an acid, the zinc salt of which is soluble. The electrodes are sheets of zinc having a surface of 1 square meter and a thickness of 1 cm. The sulphate of zinc which is formed at the anode during electrolysis is precipitated by the caustic soda formed at the cathode, with the formation of hydroxide of zinc. This compound is separated from the solution by filtration, and is then dried and calcined in order to produce anhydrous oxide of zinc or zinc white. It is preferable to use a pressure of 2.5 volts, and a current density of 10 amperes

per square decimeter, as with that current density an increase of temperature of the electrolyte is obtained, which is favorable for the precipitation of the hydroxide of zinc. The temperature quickly reaches 60 degrees C., and this is maintained by causing the liquid to circulate in the tanks. The product obtained is stated to be 1.5 grams ZnO per ampere-hour, from which a ton of zinc white in twenty-four hours is calculated to require 74 kw. or 96 chp.

**Process of Obtaining Metals.**—F. von Kuegelgen, Holcombs Rock, Va., and H. Danneel, of Breslau, Germany, assignors to the Willson Aluminium Company. Patent 771,646, October 4, 1904. Application filed July 29, 1903.

The process is based upon the electrolysis of fused sodium chloride, fused either beforehand or by the current. An apparatus suitable for carrying out the process is illustrated in Fig. 2. It shows a cell, A, divided into an anode and a cathode chamber by means of a porous partition, B. The diaphragm is said not to be essential except to prevent the alkali oxide formed at the anode from going to the cathode. The anode, C, is preferably of carbon, and the cathode, D, is of iron. Oxide of tin is introduced into the cathode chamber

if metallic tin is to be obtained. The sodium liberated at the cathode is claimed to combine with the oxygen of the oxide of tin. The tin thereupon is supposed to fall to the bottom of the chamber, while the sodium oxide formed in the above reaction settles on top of it. The chlorine is liberated at the anode and may be collected in any suitable manner. The minimum voltage which will be effective for

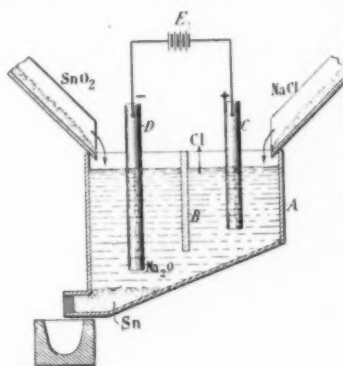


FIG. 2.—ELECTROLYSIS OF FUSED SODIUM CHLORIDE.

the above operation has not been determined exactly, but it is stated to be lower than that required for the electrolysis of sodium chloride, namely 4.2 volts. The materials may be added in continuous streams, or from time to time in considerable quantities. Whether the above reactions will take place in such a matter of fact way as assumed in the specification is much to be doubted. The electrolysis of fused sodium chloride on a practical scale is a very difficult proposition, as has been found out by various people, among them the writer.

**Apparatus for Mercurial Alkaline Processes.**—C. W. Roepper, Germantown, Pa., and W. E. Harmon, Mechanics Falls, Me. Patent 771,833, October 11, 1904. Application filed January 30, 1903.

The apparatus belongs to that type of mercury apparatus in which mercury is transferred from the compartment in which it is charged with amalgam into another one where the amalgam is discharged, after which the mercury is again returned to the charging compartment. In its construction special attention has been paid to the control and the regulation of the circulation of the mercury in order to facilitate the reactions which take place in the two compartments, and to reducing the amount of mercury required in the apparatus as much as possible. The apparatus is a rectangular box, with a so-called main partition, which divides the anode from the cathode compartment. The partition reaches down into a groove in the bottom of the apparatus, so that a complete separation of the electrolyte from the caustic solution obtained from the discharge of the amalgam is effected. It



is stated to be important that the body of mercury or amalgam in the electrolytic compartment be comparatively thin and free from any waves or agitation, notwithstanding its circulation, and that the layer of mercury move evenly forward, and, although thin, be at no point broken. The bottom of the electrolytic compartment, therefore, is so constructed that it slopes up towards the main partition, by which means the maintenance of any considerable or stationary body of mercury in this department is prevented, while the amount of the metal necessary is reduced to a comparatively thin, wedge-shaped layer. The mercury, therefore, falls down as it passes under the partition, and this prevents any waves caused by the wheel, which accomplishes the circulation of the mercury from being communicated to the mercury in the electrolytic compartment by means of the groove. The bottom of the amalgam discharging compartment slopes down towards the wheel, in order to facilitate the circulation of the amalgam, as it is not necessary that the bottom of this compartment be completely covered with it. The discharge of the amalgam is effected by a series of discharging plates. The above mentioned wheel discharges the mercury into a narrow compartment, which is connected with a canal running along one of the longer sides of the box, which canal at the other end of the box enters another narrow compartment. The latter is separated from the electrolytic compartment by a partition, reaching down into a groove in the bottom of the box, and thus effecting a mercury seal as in the case of the main partition. Both of the partitions are traversed lengthwise by a pipe which is fitted with a series of apertures opening into the electrolytic compartment above the level of the mercury and spaced across the width of the compartment. The pipe towards the discharging end of the apparatus serves for the introduction of the electrolyte, while the one towards the other end serves for its discharge. The apertures may be provided with aprons, which deflect the flow of the solution downwards. It is claimed that this arrangement distributes the flow of the electrolyte over the width of the compartment, and compels it to flow in the vicinity of the bottom edges of the anode plates, thus assisting in keeping the bottoms of the anode plates free from adherent gas bubbles. The apparatus gives the impression of being well thought out, and being based upon a thorough acquaintance with the conditions which have to be fulfilled in order to successfully accomplish the electrolysis of alkali salts with a moving mercury cathode on a practical scale.

*Electroplating Apparatus.*—Willis R. King, New York, assignor to the Hanson & Van Winkle Company. Patent 772,102, October 11, 1904. Application filed February 8, 1904.

The apparatus is designed for the plating of small articles, with a view to effect an improvement in the mechanical construction of such apparatus in general, and to accomplish the removal of the drum containing the small articles without disturbing or interfering with the driving mechanism or removing belts. The apparatus is also intended to buff or polish the plated surfaces of the articles. The drum in which the articles to be plated are contained, is made of a suitable non-conducting material, preferably of wicker work, and has the form of a basket or drum, provided with perforated wooden plates at the ends. It has a wicker work or other suitably constructed lid, provided with fastening devices. In the center of the drum there is arranged a shaft, which, by means of suitable mechanical devices is connected with the driving mechanism in such a way that it can easily be detached or inserted. A number of contacts are placed upon this shaft, which consists of a hub provided with several radially-extending straight or hook-shaped arms. The latter during the revolution of the drum are brought into constant contact with the articles to be plated, and as they are in metallic connection with the negative terminal of the dynamo by means of the central shaft and the suspension device, the

articles are made cathodes and receive the deposit. The drum is suitably suspended into the apparatus by means of a supporting frame. The anodes are placed on conducting bars parallel to the long axis of the drum.

*Electroplating Machine.*—James Bailey, Walsall, England. Patent 770,148, September 13, 1904. Application filed February 14, 1903.

The essential feature of the machine is a traveling conveyor chain, which is driven in the horizontal plane a short distance above the surface of the electrolyte. Its mechanical construction is such that it can be readily adjusted, and eyes or recesses are provided in each link in which the work to be plated may be hung. After the work is thus connected it travels up and down continuously between four rows of anodes, the combined area of which is much greater than that of the work. It is stated that the plating is obtained very rapidly as compared with processes employed hitherto, and that on account of the constant circulation the deposit is found to be smooth and perfect, and not in the least granular. When the conveyor chain is once loaded with work, the process is continuous, and as plated work is removed, fresh work may be hung on.

*Cleansing Sheet Zinc.*—John Nelson, Peru, Ill. Patent 768,818, August 30, 1904. Application filed April 30, 1903.

The invention relates to means for treating sheet zinc preparatory to plating it. The inventor proposes to accomplish this purpose by connecting the sheets of zinc which are to be cleaned as cathodes in an electrolytic bath. As anodes he uses longitudinally-corrugated sheet iron plates. The tank in which electrolysis is carried out is of wood. The electrolyte is given as being of the following compositions: 1 gallon water, one-half ounce of potassium cyanide, 1 1-3 ounces sodium carbonate and 1 1-3 ounces lye (one-third ounce NaOH plus two-thirds ounce KOH). One gallon of four F ammonium hydrate is added to 150 gallons of the above mixture. The best results are stated to be obtained with a pressure of 7 volts, and for cleansing three pairs of sheets with six exposed surfaces of 3 feet by 7 feet, a current of about 400 amperes is required. It is claimed that by subjecting the sheets of zinc to electrolytic action in a bath of the above composition, they are thoroughly cleaned without having their polish destroyed, which would take place if the zinc were to be attacked by an acid.

#### STORAGE BATTERIES.

*Secondary, or Storage Battery.*—Carroll Potter, Philadelphia. Patent 769,403, September 6, 1904. Application filed December 21, 1903.

The object of the invention is to provide for guarding against accidental detachment of the plate lugs from their connecting strap, and to facilitate the operation of connecting the plate lugs and their connecting strap. For this purpose the plate lugs are provided with lateral projections, which have beveled or chamfered ends. Two of these projections are placed in alignment and burned together, thus producing a bridge piece. The burning is facilitated by the chamfering of the ends. The strap is provided with beveled or chamfered openings, through which the lugs are inserted and then burned and puddled in order to connect them. The bridge pieces are intended to impart mechanical strength to the structure and to prevent the lugs from working loose and becoming detached at the places where they are connected with the strap.

*Secondary Battery.* Lothar Fiedler, Stoke Newington, England. Patent 770,277, September 20, 1904. Application filed June 28, 1904.

The battery is constructed out of a series of trays with sloping sides, each being immersed into the one next below, with its bottom well below the level of the electrolyte contained in the lower one. The trays are shallow and composed of thin metal of an acid resisting nature, preferably lead. A lining is laid on the bottom of the trays, which consists of a

paste formed of finely divided zinc thoroughly amalgamated with mercury. The lining forms one electrode of the battery. Above the lining there is arranged an insulating support, composed of a corrugated and perforated plate of vulcanite, celluloid or similar material. This serves as support for a plate, which forms the positive pole of the battery, and which consists preferably of a lead grid, the spaces of which are filled with a paste of peroxide of lead. The electrolyte may be in a liquid or in a gelatinous condition. This construction is claimed to have the advantage of overcoming the disintegration which makes its appearance when vertical zinc

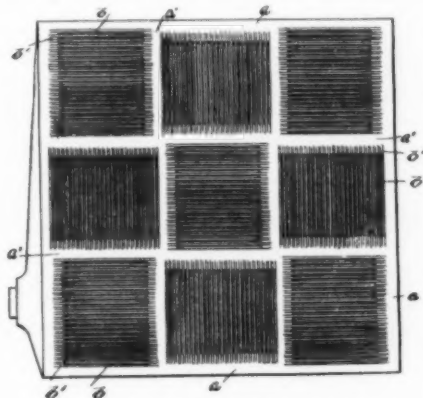


FIG. 3.—STORAGE BATTERY PLATE.

plates are employed, and which is due to the tendency of the amalgamated zinc to gravitate toward the lower portion of the plates, a tendency which is further promoted by the tendency of the zinc deposit on the plate, when the battery is charged, to be spongy.

*Electrode for Batteries.*—A. C. Wood and J. A. McMullen, Philadelphia. Patent 770,140, September 13, 1904. Application filed April 22, 1902.

The electrode is illustrated in Fig. 3. It comprises a sufficiently rigid framework, *a*, of lead or other suitable material, and a series of thin lead strips, *b*, arranged parallel to each other, and in groups separated from each other by means of the cross-pieces, *a'*. The lead strips are spaced apart in order to insure a free circulation of the electrolyte and in order to facilitate their proper and uniform spacing apart, and to render it easy to set them in the mold, the end portion of each strip is bent back upon itself, as indicated at *b'*. It is claimed that if a number of strips thus formed be arranged on edge and grouped together, they will support and properly space one another, and there is no necessity therefore of employing skilled workmen to set the strips and specially-devised molding apparatus to hold them. Adjacent groups of strips are disposed at right angles to each other. The strips *b* are notched at their ends, the notches being formed preferably in the thickened portions, and when the strips are set on edge, these registering notches form a channel which communicates with that of the adjacent group of strips. When the fluid metal is then run into the mold, the metal runs freely into the channel, and, fusing together with the contiguous portions of the ends of the strips, causes a perfect union of them. At the same time the fluid metal cannot enter the spaces between the strips, as the thickened ends of the latter abut closely. It is claimed that the spaces between the outermost strips of each group and the adjacent ribs are substantially the same as those between the strips themselves, and that the comparatively large open spaces, which have been incident to electrodes of this character, are thus entirely avoided.

*Cell for Storage Batteries.*—P. Figuccia, Boston. Patent 770,358, September 20, 1904. Application filed February 19, 1904.

The cell is rectangular in shape and provided with a lining

of rubber, glass, etc. It is divided into a series of compartments by upright partitions of non-conducting material; the nature of the material is not stated. In each of these compartments are placed an anode and a cathode, which are kept apart by the interposition of a flat separator of thin wood, etc. The idea underlying the construction is the prevention of short-circuits caused by active mass dropping from the plates.

*Lead Containing Cell for Secondary Batteries.*—V. G. Apple, Dayton, Ohio. Patent 772,123, October 11, 1904. Application filed June 3, 1903.

The cell is made in one piece, and is provided with a number of parallel vertical interior ribs, which are integral with the walls and serve to receive and retain the active mass. The cell is made by softening lead and then forcing it into a mold under pressure. The inventor has found that it is possible to cast the lead in the softened condition which it assumes just before reaching the fusion point (approximately 620° F.), by employing a sufficiently great pressure. With the lead in a molten condition a pressure of 120 pounds per square inch produces good results for small cells, but the larger the cell to be cast, and the thinner the walls, the greater the pressure that must be employed. The inventor states that he is enabled to produce in this manner cell walls of much less thickness and correspondingly less weight than any other process of manufacture, as the cast wall can be made extremely thin,

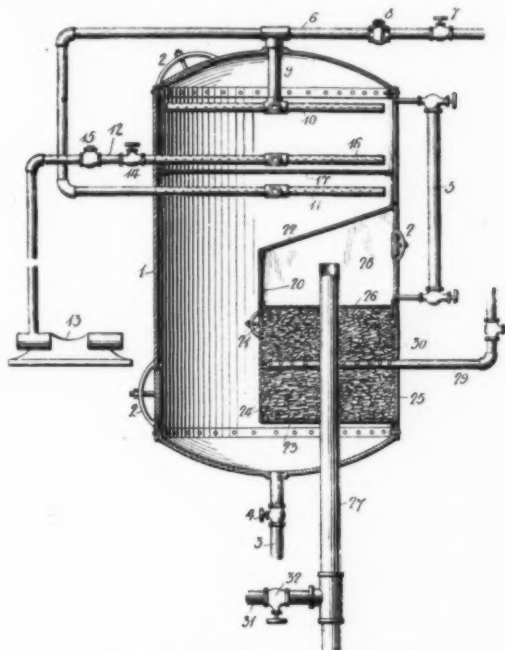


FIG. 4.—FEED WATER PURIFIER.

the density of the wall preventing the formation of blowholes. He claims to be making cells now, the thickness of whose walls does not exceed 1/32 inch.

#### MISCELLANEOUS.

*Feed Water Purifier and Filter.*—W. Dougherty, Chester, Pa. Patent 769,792, September 13, 1904. Application filed October 17, 1903.

The apparatus is illustrated in Fig. 4. It consists essentially of a drum 1, with hand holes 2 and provided with a steam pipe 6 and feed-water entrance pipe 12. A perforated diaphragm 17 is arranged within the upper part of the apparatus, which is made of equal parts of nickel and zinc, wherein the nickel is for the purpose of preventing a too rapid wasting away of the zinc. Other metals may be employed, but nickel is said to give the best results. It may also be made of galvanized

iron or woven wire heavily coated with zinc. The perforated cross 16 on pipe 12 is either entirely of copper or of iron, coated with copper. The galvanic action between the copper and the zinc is claimed to considerably increase the deposition of the solids held in solution or carried mechanically by the feed water. A filter box 20, filled with crushed flint or other non-absorbent filtering material 25, is supported upon the inside of the drum, and has a perforated bottom 23 and sides 24. The upper walls 20 and the top 22 are solid. The water passes through the filtering material and the perforated plate 26 into the upper part of the filter box, whence it is drawn off in a purified condition through boiler feed pipe 27. A perforated steam pipe 29 serves to clean the filter.

*Water Purifier.*—F. G. Kuné, New York. Patent 769,750. September 13, 1904. Application filed December 19, 1903.

The apparatus consists of a casting with an upper inlet and a lower outlet passage, which passages are connected by a number of tubular conduits. The whole is connected to one pole of a source of current. A cylindrical electrode is introduced through an insulating bushing into each of the above

conduits. These electrodes are all connected to the other pole of the source of current. The water to be purified flows through the space between the cylindrical electrode and the conduit wall, and is subjected to electrolytic action.

*Water Purifying Apparatus.*—F. G. Kuné, New York. Patent 769,749, September 3, 1904. Application filed November 5, 1903.

The apparatus differs from the preceding, inasmuch as the successive conduits form a single line of pipe, each conduit being provided at its upper end with a T and at its lower end with an elbow. The tee of the first pipe is connected with the inlet pipe, and that of the last one with the outlet pipe, the tees, as well as the elbows of the intermediate ones, being connected by means of nipples. The pipes are parallel and preferably arranged vertically. An electrode is introduced by means of an insulating bushing into each of the pipes, and the water, as it flows through the system of pipes, comes successively under the electrolytic action between these electrodes and the walls of the pipes, the latter being connected to the other pole.

## RECENT METALLURGICAL PATENTS.

### METALS AND FERRO-ALLOYS FREE FROM CARBON.

It is well known that if carbon is used as a reducing agent for the reduction of metallic oxides for the purpose of producing either the pure metal or a ferro-alloy, the latter are never obtained free from carbon. It is, of course, possible to use somewhat less carbon than is theoretically required for reduction and to thus keep the content of carbon in the product down. But this has the disadvantage that part of the oxide which was to be reduced is lost, is slagged off; at the same time if the process is carried out in an electric furnace with carbon electrodes, the oxygen of the oxides exhibits its affinity for the latter and an unduly high consumption of electrodes results.

H. Goldschmidt has applied the most radical remedy, namely, to use aluminium, instead of carbon, as reducing agent; then no carbon can, of course, get into the product. In a quite different manner F. von Kügelgen and G. O. Steward (U. S. patent 771,645, October 4) try to overcome the difficulty. They conduct the electric furnace process in such a way that all the oxide is reduced and that the consumption of the carbon electrodes is a minimum; in other words, they do not care at first how much carbon they get in their product. But then, while their metal or alloy is still molten they bring it in contact with metallic calcium. This may be done by putting metallic calcium in the bottom of the tapping mold and tapping the furnace product onto it, or the calcium may be added while the metal is still in the original furnace. The calcium, by reason of its great affinity for carbon, forms calcium carbide which separates from the metal while the metal is still molten, and which rises to the top and is removed as slag. There is usually a small quantity of oxygen in the metal, and this will oxidize a part of the calcium, leaving only the remainder to unite with the carbon. It is, therefore, advisable to use an excess of calcium over that necessary to extract the carbon from the metal, the excess being proportioned to the oxygen content of the metal.

If the process should prove useful on a large scale, it would open the path for a new electrochemical product—metallic calcium; for there can be no doubt that calcium, like aluminium, will require for its manufacture an electrochemical method. Such methods were already noticed in our Vol. I, page 104, 143, 418, 422 and Vol II, page 276.

C. E. Manby (771,559, October 4) patents a steel alloy for

which he claims great tensile strength, ductility and resiliency, and which is said to be particularly adapted for the manufacture of wire for musical instruments. Claim 1 reads, "as a new article of manufacture, steel containing nickel and ferrovanadium." The best composition is given as follows: "Iron, 78.10 per cent; nickel, 20 per cent; ferromanganese, 1.28 per cent; ferrovanadium, 0.62 per cent."

### UTILIZATION OF WASTE FURNACE GASES.

The utilization of waste furnace gases is attracting more and more attention. The problem is to turn them to the best advantage in any given case. It was recently pointed out by W. R. Ingalls that processes which throw away great quantities of apparent value are not necessarily wasteful because they do so. Thus the waste of sulphur in burning sulphide ores is a waste if there is a market for sulphuric acid where such ores are smelted; but if there is no market, it may not be a waste at all. The utilization of the waste gases from blast furnaces for driving gas engines coupled to electric generators is now practiced on a large scale, especially in Europe; and there can be no doubt that in blast furnace works electrical energy is under all circumstances a most valuable by-product.

J. Herman (769,263, September 6) remarks that in copper matting and lead blast furnace practice at least three-quarter down to two-thirds of the carbon in the charge is burned to carbon monoxide; he proposes to pass the furnace gases through or over metallic oxides, such as roasted ore, in order to reduce the metallic oxides either to lower oxides or to the metallic state and oxidize the carbon monoxide to dioxide. "When desirable, the ore may then be reoxidized by the admission of air, and thereby adapted to do its work continuously for an indefinite period." The heat generated by the oxidation of the carbon monoxide may be used for heating air blasts for furnaces or for heating boilers, etc.

Even if the process can be made to work as the inventor desires, the figures given by him for the available heat are too high, since he entirely overlooks that energy is necessary for the reduction of the oxides.

### ORE DRAINING AND LEACHING TANK

J. F. Webb (772,389, October 18) patents a tank for the rapid collection, drainage and treatment of slimes in cyanide mills, the particular object being to obviate the use of a filter process in the final treatment of slimes pulp. For this



purpose he uses a drainage and leaching tank having double walls and bottoms with an annular space between them, the outside shell having solid sides, top and bottom, with openings in it so arranged that it can be made air and water tight when under pressure, and the inner shell having its sides and bottom perforated and covered with suitable filtering material. Inside of the double walls and preferably in the center is a much smaller secondary hollow compartment or pressure stand-pipe, which is also perforated and covered on the outside with suitable filters to prevent it from being filled with slimes during the filling of the tank. This central pressure stand-pipe is connected at the top with hydraulic pressure pipes supplying either solvent solution or wash water, as required. It is also so arranged that the fluid pressure can be cut off and compressed air introduced into it and used in forcing the liquid contents in the pulp contained in the tank outwardly and downwardly through perforated sides and filtering material into the annular space between the sides and bottoms.

After separation from the sands, the slimes are run directly into the tank shown in Fig. 1, through the filling pipe 1. The liquid contained in the slimes then drains out through the filtering materials 3 and 4 and the perforated inner shell 5, and is caught and held in the annular space between the inner shell 5 and the solid shell 6, whence it runs out through the drainage pipes 7 and 8, and is pumped back to the usual storage vat. The filters 3 and 4 prevent the slimes from running through with the liquid, and they settle on the bottom of the tank until the latter is filled. The supply is then cut off and fresh cyanide solution is admitted into the central pressure stand-pipe tank. This is continued until the values are all dissolved, when the supply of solution is cut off. When the leaching is complete, compressed air is admitted into the perforated pipe tank, which results in compressing the pulp and squeezing out the solution. Wash-water is then admitted through pipe 10, and finally the leach pulp is discharged through the valves 17 and 18, in the bottom of the tank.

In amalgamating mills where the ore is crushed in clear battery-water, the tailings or slimes, after passing over the plates and concentrators, are run into the tank, the battery-water is washed out of them by compressed air, the solution admitted to the pressure stand-pipe, and the leaching and washing is proceeded with as described.

#### MISCELLANEOUS.

O. Massenez (772,164, October 11) patents a process of decromizing iron, in order to make it malleable. The main point is that when the metal is exposed to an oxidizing flame in the open hearth furnace, the chromic acid formed is absorbed by a slag which is easily fusible by itself, and that the amount of this slag is so proportioned that it contains less than 13 per cent of the chromic oxide.

G. L. Smith (771,675, October 4) patents details of construction of a crucible furnace with the use of gas or oil as fuel and the utilization of some portion of the waste heat in the waste gases.

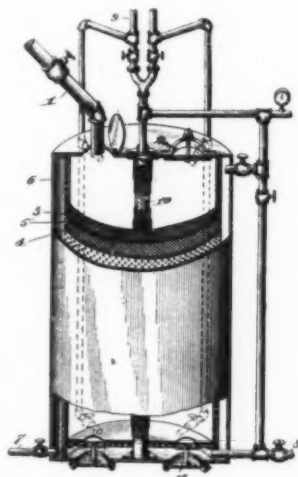


FIG. 2.—LEADING AND FILTERING TANK.

J. A. Potter (769,712, September 13) patents an endwise-tilting furnace which is always connected at its higher and lower ends with the fuel supply and regenerator fuels, so that the higher portion of the furnace end and bottom are always exposed and highly heated.

J. Gayley (771,058, September 27) patents details of construction of apparatus for extracting moisture from air for blast furnaces or converters. The air is artificially cooled.

J. G. McGee (769,665, September 6) describes details of construction of a smelting furnace, with respect to water jackets surrounding the furnace, a wind jacket for supplying air to the interior of the furnace, and a water jacket for surrounding the slag spout.

J. W. Arnold (768,576, August 30) patents details of construction of a heating furnace by which the billets and bars of metal to be heated or re-heated are mechanically charged into the furnace, and can thus be charged either hot or cold.

A. Latta and J. C. Callan (772,723, October 18) provide means in connection with blast furnaces for catching and collecting the dust, dirt and fragments of ore which are discharged from the top of the furnace by the explosions incident to the operation.

M. Corcoran (769,689, September 13) patents details of construction of rabblers for use in calcining or roasting furnaces, in order to render the renewal of parts easy.

Feeding devices are patented by S. Forter (767,399, August 16, distribution of the charge for gas producers, blast furnaces, etc., toward the center and the sides); W. R. Reese (770,111, September 13, even distribution of the charge within a blast furnace); J. Roger (770,701, September 20, continuous and automatic feeding of ore to roasting furnaces); S. W. Vaughn, J. B. McClure and A. J. Boynton (768,207, August 23, blast furnace, top construction); and W. H. Freeland (768,596, August 30, delivering the ore or charge from stock piles, bins or bunkers to a point directly over the furnace).

F. O. Stromborg (771,681, October 4) patents a water-seal valve and valve-operating apparatus for regenerative furnaces; S. Stewart (772,846, October 18 a gas seal for metallurgical furnaces.

L. Silcott (768,546, August 23) described details of construction of a twyer iron; L. Keyling (770,910, September 27) a device for cooling the top gases, extinguishing the top flame and sparks and keeping the ashes back in blast furnaces. F. McCarthy (769,106, August 30) patents means for controlling and actuating the "notch-gun," whereby a single attendant may easily stop the "iron-hole" in a blast furnace after each cast.

C. Barber and G. L. Chase (769,584, September 6) patent details of construction of a waste trap for saving the precious metals contained in jewelers' waste.

O. S. Still (770,127, September 13) describes details of construction of a condenser for extracting mercury from ores.

## Current Notes.

**ARTIFICIAL RUBIES.**—According to a recent consular report, artificial rubies are made by a process of the chemist Verneuil, by melting a mixture of clay and oxide of chromium at an even temperature of several thousand degrees. The two substances are carefully placed above each other in layers so as to prevent cracking the crystallized mass. It is stated that Verneuil finally succeeded in producing an artificial ruby weighing 5 pounds, which had a value of about \$600. From this price it may be judged that the product is not first class, and probably just pays the costs of manufacture. In order to produce the exceedingly high temperature which is indispensable for success, Verneuil uses a blast of oxyhydrogen gas, which acts directly on the mass from the top. The hardness of the

ruby is the result of quick cooling caused by sudden interruption of the blast of oxyhydrogen. The artificial ruby is said to be very pure and brilliant, possessing all the physical properties of natural rubies. It can be cut, and takes a very fine polish. In this connection it may be mentioned that, in the manufacture of pure chromium by reduction with aluminium according to Goldschmidt's method, sometimes small crystals of rubies are formed. There is, of course, nothing surprising about this, since the ruby is corundum, colored red by traces of chromium.

**PHILADELPHIA SECTION AMERICAN ELECTROCHEMICAL SOCIETY.**—The Philadelphia members of the American Electrochemical Society held an informal meeting on October 7th, at the hall of the Engineer's Club, of Philadelphia, to discuss the arrangement of Section meetings for the winter. It was thought that a series of meetings "of the smoke-talk and 'round-table-talk fashion," would be the best plan for the coming season.

**AMERICAN INSTITUTE OF MINING ENGINEERS.**—We have received from the Secretary's office package No. 5, 1904, of Institute pamphlets. It contains the following papers: H. M. Chance on the Taviče Mining District near Ocotlan, State of Oaxaca, Mexico; J. M. Clements on the Manufacture of Coke in Peru; E. A. Hersam on Testing Gold Ores by Amalgamation; S. H. Loram on the Gold District of Canutillo, Chile, S. A.; K. V. Norris on Centrifugal Ventilators; A. C. Spencer on Geology of the Treadwell Ore Deposits, Douglas Island, Alaska; G. F. Williams on the Genesis of the Diamond, and biographical notices of William Henry Pettee and Robert Henry Thurston, both being written by Dr. R. W. Raymond.

**NEW CARBON COMPOUND.**—At a recent meeting of the French Academy of Sciences, M. Henri Moissan presented a paper concerning the preparation and characteristics of a new carbon compound containing molybdenum. According to a recent consular report, this compound is obtained by heating charcoal with melted molybdenum and aluminium in an electric furnace. The resultant metallic mass is treated with a concentrated solution of potash, and needles of well-defined crystals of the new carbon compound are obtained. The substance is very hard, is hardly attacked by acids other than nitric, and is not decomposed by water or steam at a temperature below 600° C. It resembles the carburet of tungsten, already known. It is thought that this new compound may play a role in molybdenum steels.

**PROPOSED AMERICAN STEEL PLANT IN CANADA.**—It is reported that the United States Steel Corporation is seriously considering the establishment in Canada of a large plant for the manufacture of steel rails and steel generally. Its agents are collecting data regarding output, consumption, etc., as well as selecting a location for the proposed works. When this work is finished the question will be settled. The new duty of \$7 a ton on steel rails completely shuts out the American rail manufacturers, and as the Canadian market is becoming a very important one the only way out of the difficulty is to build a manufacturing plant in Canada. Experts say that a plant such as the Steel Corporation would like to put up would cost from \$12,000,000 to \$13,000,000.

## Book Reviews.

*Electrical Influence Machines.* By John Gray, New York: D. Van Nostrand Co. Price \$2.00.

This book is a very complete description of the modern influence machines. The first part devotes itself to electro statics, while the influence machines are fully described in the second part. The author gives special attention to the modern ma-

chines and describes fully Varley and Toepler's, Holtz's, Wilmhurst's, Lord Velvin's, Pidgeon's and compressed air machines, which are at the same time amply illustrated. The third section is devoted to the practical construction of Wilmhurst's and Holtz and Voss's machines, the illustrations of this section being very complete and dimensioned.

### ELECTROLYTIC PRODUCTION OF PHOSPHATE FERTILIZERS.

On page 65 of our first volume (October, 1902) we noticed a process by Wiborgh and Palmaer for manufacturing manure from apatite, or similar mineral phosphates. Further developments in the same direction are recorded in a pamphlet issued by Dr. WILHELM PALMAER, from which the following information is taken. Dr. Palmaer is the director of the electrochemical laboratory of the Technical College of Stockholm, Sweden. The pamphlet is an account of his "electrolytic process for producing bicalcic phosphate for use as a fertilizer out of unserviceable raw phosphate."

It is a well-known fact that large quantities of raw phosphate occur, which are not available for the production of superphosphate, either by reason of their low percentage of phosphoric acid, or on account of other drawbacks attaching to them. That is the case with phosphorites and apatites containing less than 50 per cent of tricalcic phosphate, also with raw material containing a high percentage of iron, whether the iron occurs in combination with phosphoric acid or in the form of magnetite or haematite (in products of magnetic separation). The object of the Palmaer process is to produce at a profitable rate a satisfactory phosphoric acid fertilizer out of the above indicated raw products. The following data are stated to be derived from the experience gained with an experimental plant of a capacity of 6 to 8 electric horse power. The general features of the method are described as follows. "In an apparatus expressly adapted for the method, a solution of chlorate or perchlorate of sodium is electrolyzed. In the anode chamber an acid is thereby generated—chloric or perchloric acid—and in the cathode chamber a solution of caustic soda. The electrolysis is continued until a certain quantity of the dissolved salt has been separated into acid and alkali. The anode and the cathode solutions are led off into separate receivers. The acid anode solution is then allowed to work in a dissolving battery upon raw phosphate, in which process the phosphate is dissolved. Into the solution thus obtained the alkaline cathode solution is introduced, the whole being meanwhile kept vigorously stirred, until the liquid bears evidence of a slightly acid reaction; to obtain that result about half the cathode solution is required. In the process bicalcic phosphate is precipitated as a finely crystalline precipitation, which is drained off by filtration and washed. The filtrate, which contains 1-3 of the lime originally dissolved, but hardly any phosphoric acid, now had added to it the remainder of the cathode solution, whereupon the greatest part of the lime in the solution is precipitated as hydrate; by the introduction of some carbonic acid the rest is precipitated as carbonate; the lime precipitation is allowed to settle. The solution remaining above it is then drawn off. The original electrolyte is regenerated by its means and again enters the electrolyzing apparatus."

The process has been applied to the treatment of both phosphorites and apatites of various origin. The percentage of phosphoric acid varied between 9 and 40, corresponding to a variation of from 20 to 88 per cent of tricalcic phosphate, without having any effect on the course of the process. The raw material must be sufficiently pulverized, so that no grains of phosphate are embedded in silicates or other insoluble minerals.

"Out of the amount of acid generated per ampere-hour, 1.33 grams of tricalcic phosphate are stated to be dissolved. The voltage required is given as about 5 volts per cell. The phosphoric acid remaining in the solution after the precipita-

tion of bicalcic phosphate is about 1 per cent of that present in the raw material.

"Of the silicates or iron ore (oxides of iron) mingled in the raw phosphate, no appreciable quantity is dissolved. If the raw phosphate contains carbonate of lime, it is dissolved by the acid simultaneously with the phosphate, chlorate (perchlorate) of lime and carbonic acid being formed and the latter disappearing; consequently, the consumption of acid is rendered greater by the presence of the carbonate of lime, which is, from an economical point of view, a disadvantage. In this process one percent of carbonic acid in the raw material involves practically the same amount of consumption of acid, or of energy, as one per cent of phosphoric acid. On the subsequent addition, however, of the alkaline cathode solution, the same high-percentage bicalcic phosphate is precipitated. Consequently, an equally excellent fertilizer is obtainable out of raw phosphate containing carbonate as out of that free from it, though at an expenditure of more acid, or of more electric current. In any case, by the electrolytic method it will be possible to make use of raw phosphates containing more carbonate than is the case in the manufacture of superphosphate; on the other hand, they are not the most suited to be first resorted to."

With reference to the electrolyte to be used, the inventor states that it should be of such a nature that its acid (formed anodically) may yield, in conjunction with lime, an easily soluble salt, and of a kind which is not subject to change during electrolysis. "As electrolyte, solutions of perchlorate of sodium or chlorate of sodium are suitable, or else mixtures of those salts; the presence in small quantities of other salts, for instance chloride, is of no account. Both these salts are thoroughly suited to the purpose, perchlorate of sodium being the best that could be desired. Both chlorate and perchlorate of sodium are exceedingly easily soluble salts—1 part of chlorate of sodium being soluble in 1.05 parts of water at an ordinary temperature, while perchlorate of sodium is still more easily soluble; that is of importance, inasmuch as the washing of the precipitated bicalcic phosphate is thereby rendered considerably easier. A slight loss of the electrolyte by spilling in the process of washing, etc., always occurs. The amount of that loss will not exceed a value of \$1.50 per ton of the finished article if perchlorate is employed."

The normal percentage of citrate-soluble phosphoric acid ( $P_2O_5$ ) contained in the bicalcic phosphate produced by the electrolytic method, is stated to be about 34—irrespective of the character of the raw material. As the quantity of citrate-soluble phosphoric acid in the bicalcic phosphate obtained constitutes about 95 per cent of all the phosphoric acid in the product, the total percentage of phosphoric acid in the bicalcic phosphate works out at 35.8 on an average.

An account is given of experiments carried out by Prof. H. G. Söderbaum, chemist to the Swedish Royal Academy of Agriculture, with respect to the efficiency of electrolytic bicalcic phosphate as a fertilizer. The result of his experiments in cultivation is that the citrate soluble-phosphoric acid in the bicalcic phosphate proves to possess the same fertilizing value as the water-soluble phosphoric acid in the superphosphate, and consequently the same value as a trade product. Bicalcic phosphate can be employed as a fertilizer on all kinds of soil, even on sandy and boggy land, where superphosphate is out of the question. Bicalcic phosphate is also considered to be of excellent use in the manufacture of "complete fertilizers." Retrogradation of soluble phosphoric acid in the bicalcic phosphate, when stored, does not occur.

The question of cost of the process is, of course, of decisive importance. In this respect Dr. Palmaer gives the following data. 'One electric horse power produces in a year: 1.73 ton bicalcic phosphate, containing 36 per cent of soluble phosphoric acid; or 1.95 ton bicalcic phosphate, containing 32 per cent of soluble phosphoric acid.

"The percentage of soluble phosphoric acid will vary be-

tween 32 and 36 per cent, depending on the degree of desiccation, etc. But under given circumstances a product of uniform composition will be obtained with a percentage of phosphoric acid from 32 to 36 per cent. Ninety-five per cent of the total phosphoric acid will always be citrate-soluble. The cost for chemicals is small as they are regenerated. As a by-product will be obtained about one-half ton of very good lime for every ton of bicalcic phosphate.

"The capital needed amounts to about \$65 per e. h. p. used in the manufacture, a plant of at least 2000 e. h. p. being supposedly employed. For manufacture on a larger scale the capital needed will be proportionately smaller. In this calculation it is supposed that the electric power is hired, and consequently the cost for the electric power plant is not included."

These last statements are not quite clear, but it would appear from this, that the figure, \$65.00 per e. h. p., represents the first cost of installation and does not include the cost of operation. Of the latter, the cost of power would probably be an important item which may be calculated from the above data on the output of fertilizer per hp.-year. There would also be expenses for handling the material, etc., which cannot be exactly estimated from the data of the author. He points out that the freightage for a given quantity of phosphoric acid in the finished product is only about half that in the case of ordinary superphosphate.

A collection of samples of raw materials and products of this process is exhibited at the St. Louis Exposition in the Mines and Metallurgy Building, in Block 13.

#### PYROMETERS SUITABLE FOR METALLURGICAL WORKS.

(Continued from page 431.)

In the discussion of CALLENDAR & GRIFFITH'S pyrometers, thermo-couples, etc., in our last issue (page 432) the consideration of the resistance thermometer and its use for reading temperatures directly were described.

For recording temperature by means of an electric-resistance thermometer a Callendar recorder is employed. This instrument, which was designed by Prof. H. L. Callendar, consists of a Wheatstone bridge or potentiometer, in which the movements of the slider along the bridge wire is automatically effected by relays worked by the current passing through the galvanometer between the bridge-arms. According as the moving coil of this galvanometer is deflected in one direction or the other, a relay circuit is connected through one or the other of two electromagnets. Each of these magnets is mounted on a clock, the movement of which is prevented by a brake. When a current passes through a magnet this brake is lifted, allowing the clockwork to revolve. These clocks are connected by differential gearing with a recording pen, which is pulled in one direction or the other when the brake is lifted from the corresponding clock. The bridge slider moves with the pen and tends to restore balance. The thermometer employed in connection with the Callendar recorder is specially designed for measuring the temperature of annealing furnaces, and the recorder can be used for the determination of recalcitrant points, either by means of resistance or thermo-electric pyrometers. The direct-reading thermo-electric instrument consists of a sensitive D'Arsonval galvanometer, the coil of which carries a pointer reading on a scale divided in degrees Centigrade. By means of a simple switchboard several thermo-couples can be connected in turn with the galvanometer. The Callendar & Griffith's instruments are sold in this country by James G. Biddle, of Philadelphia.

3. *The Le Chatelier Pyrometer.*—At the instance of the Royal Physical Technical Institute at Charlottenburg, Mr. W. C. Heraeus, of the firm of platinum refiners at Hanau, undertook the manufacture of a pyrometer according to the



principle of Prof. Le Chatelier, of Paris. The principle involved in the conversion of heat into an electric current and the determination of the degree of heat by a suitable device indicating the e. m. f. of such a current. A decided advantage which this pyrometer possesses over all others consists in its ease of application and convenience in handling, and in the fact that the temperature can be read off at almost any distance from the source of heat. The following is a description of the apparatus and of the method of operation: Two wires, one of absolutely pure platinum and the other consisting of the same metal alloyed with 10 per cent of rhodium, are fused together at one of their ends in the shape of a small ball (Fig. 1), and thus form a couple. This

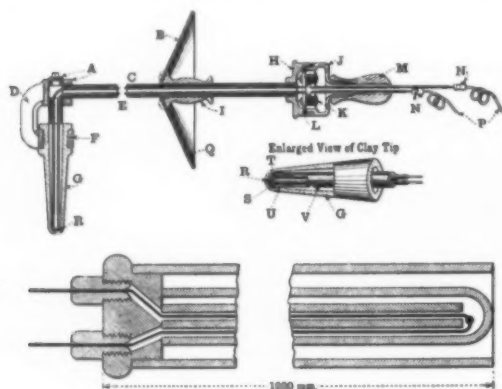


FIG. 1.—LE CHATELIER PYROMETER.

- |  |  |
|--|--|
| A. Interchangeable for Angular or Straight Connection.                                   | J. Terminal Box Cover.                     |
| B. Hand Screen.  | K. Binding Posts.                          |
| C. Platinum.   | L. Hard Fibre Disc.                        |
| D. Clamp.  | M. Terminal Box Handle.                    |
| E. Platinum Rhodium.   | N. Wire Connector.                         |
| F. Hinged Cap locked by Cam Lever, quickly opened and closed for interchanging Clay Tip. | P. Copper Wires connected to Galvanometer. |
| G. Fire Clay.  | Q. Asbestos Lining.                        |
| H. Terminal Box.   | R. Junction of Wires.                      |
| I. Hand-screen Handle movable on Pipe.   | S. Platinum Wire.                          |
|  | T. Platinum Rhodium Wire.                  |
|  | U. Internal Asbestos Lining.               |
|  | V. External Asbestos Lining.               |

ball generates a slight electric current when heated, and, as ascertained by the Royal Physical Institute, by comparison with their celebrated air thermometer, such currents are proportionate to the heat applied. Each element is accompanied by a table of results determined in the same manner. To prevent injury to the wires by abrasion, injurious gases, and by alloying with other metals, they are usually enclosed in porcelain tubes, a small tube open at both ends being used to insulate the two wires and a large one, closed at one end, covering the whole. The Royal Porcelain Factory at Berlin prepares such tubes from an extremely refractory porcelain base, which resists a temperature of 2920° F. or 1600° C. These tubes can be made up to 50 inches in length. The galvanometer used in connection with the pyrometer is of the D'Arsonval type, and is especially adapted to the measuring of thermo-currents. The current is transmitted to an armature, wound in quadrangular shape, through a fine wire of hard metal which does not oxidize. A small spring of the same material acts as a negative. A strong permanent magnet with iron pole shoes constitutes a magnetic field, and an iron cylinder in the center concentrates the magnetic lines of force. The pointer moves over two scales, one of which denotes the e. m. f. of the current in micro-volts, thus making it possible to check the readings of the instrument, while the second scale gives direct readings of the degrees of temperature. On the side of the cylindrical casing of each instrument there is provided an adjustable thumbscrew, which secures the armature, thus avoiding the breaking of its delicate suspension wire while in transit. The LeChatelier pyrometer is sold in this country by the representative of W. C.

Heraeus, Mr. CHARLES ENGELHARD, New York City, as well as by Messrs. EIMER & AMEND, New York City, and the SCIENTIFIC MATERIALS Co., Pittsburg.

(To be continued.)

#### LEAD-LINED VALVE IN BRASS CASING FOR HANDLING ACIDS.

The Schutte & Koerting Company, of Philadelphia, manufacture and have quite extensively in market a valve for the purpose of handling acids and other chemical solutions. It possesses all the features and merits that modern design can give.

The construction of the valve consists of a brass case, lined with lead, a yoke cover and spindle made of the best mixture of copper and tin; all parts being covered with lead which come in contact with the liquid.

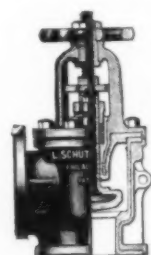


FIG. 1.—LEAD-LINED VALVE.

The valve is operated by a hand-wheel and spindle, the movement of the latter being straight up and down only. It is kept from turning by a slide fastened to the spindle, guided on the ribs of the yoke cover and a square milled on the spindle itself.

A stem nut is also provided and held in place by a jamb nut and shoulder. This stem nut revolves in yoke giving the spindle of valve its upward motion. As the stem is guided centrally at all times, there is no wear on these parts, however much the thread may wear. The upward motion, only, of the stem enables the valve to seat itself on the same identical spot at all times, thus reducing the wear and tear by friction to a minimum.

The process of molding these valves enables a smooth, uniform and uninterrupted surface to be obtained without further



FIG. 2.—LEAD-LINED VALVE, USED IN A STRAIGHT PIPE LINE.

turning or finishing. The angle form of valve only is made, as shown in Fig. 1; while, when used in a straight pipe line it is conveniently attached, as indicated by Fig. 2.

#### DYNAMOS FOR ELECTROPLATING AND ELECTROTYPING.

The accompanying cuts illustrate a line of dynamos for the electrodeposition of metals, which the Bennett & O'Connell Company, 97-101 South Clinton Street, Chicago, Ill., has brought out.

The cuts illustrate a double commutator machine of 2000 ampere capacity, at six volts, running at a speed of 550 r. p. m. This type is built in sizes ranging from 1500 to 4000 amperes, and can be furnished with double voltages when so desired. The machines of smaller capacity are of the same general design, but have only one commutator. While the standard windings are for five volts, but can be furnished with a range of from 3 to 10 volts, and by means of special windings, any voltage up to 25 volts can be obtained. The machines are of slow speed design, and built for continuous duty, under a normal rise in temperature.

The magnet frames are of cast iron, of high permeability, with round poles of the best grade of forged steel, cast welded onto the frames, and are provided with cast iron shoes which serve to hold the field windings in position and to better distribute the magnetic flux over the surface of the armature, at the same time assisting in sparkless commutation, which is one of the features which the manufacturers claim.

This line of machines is compound wound, and operate at a perfectly uniform voltage from no load to full load without the customary shifting of the brushes to accomplish this result, and insuring a uniformity in the deposit on the articles which are being plated, thus avoiding the close attention of the operator otherwise necessary in order to accomplish this result. The compound windings consist of solid copper conductors and are mounted only on the two horizontal poles, while the shunt windings are uniform in size and strength and are provided on all four poles.

The armatures are of the ventilated type, with barrel windings, the core being formed with thin discs of sheet steel, of

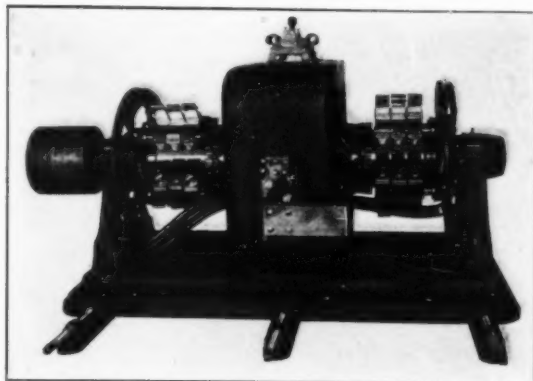


FIG. 1.—ELECTROPLATING DYNAMO.

the best electrical quality, slotted on the outer periphery for the reception of the windings. The commutators are made of rolled copper bars, uniform in thickness and temper, which is a strong point in favor of sparkless commutation. The bars are held firmly in position by heavy cast iron flanges, in which no bolts are used, so that there is no tendency to work loose by expansion or contraction. The brush holders are of neat construction, so that they clamp the brushes firmly in the holders; they are also securely fastened to the stems and the brushes can be readily adjusted independently.

The brushes are of the laminated copper type, and do not cut the commutator. The construction of the rocker arm is

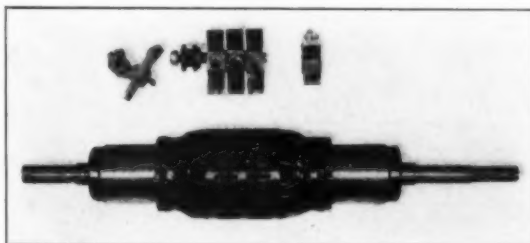


FIG. 2.—DETAILS OF CONSTRUCTION.

such that any individual set of brushes can be removed without disturbing either of the other sets. They are provided with cross-connections of solid copper bars, which are insulated from each other.

The striking feature in the design of these machines is the generous use of copper in all the parts carrying current, and the generous ratings in ampere capacity. The machines operate continuously under full-load capacity without injurious rise in temperature and without sparking in the brushes. They are tested up to 50 per cent overload for periods of from three to five hours, and are strong and substantially built.

These machines have oil reservoirs with ring oilers, which require little or no attention, and are provided with field-

regulating rheostats, mounted directly on the frame of the machine, so that when they are driven it is only necessary to make the line connections and the machines are ready for service.

## INDUSTRIAL NOTES

**THE AMERICAN SLATE COMPANY**, of Boston, Mass., have removed to more commodious offices in rooms 629-632 Board of Trade Building, 131 State Street.

**PRICES OF PLATINUM.**—It is reported that the prices of crude platinum have been very materially affected by the drafting of the laborers from the Ural mines, owing to the Russo-Japanese war, and, notwithstanding recent advances, a further rise in prices seems almost assured.

**CALCIUM CARBIDE.**—According to the London *Electrical Review*, of September 30, the Usines Electrochimique de Halfslund is the title of a new company which has been registered at Geneva, with a share capital of \$240,000 for the purpose of acquiring and working a calcium carbide installation at Halfslund, Norway. The composition of the Board of Directors shows that the Schuckert Co., of Nuremberg, Germany, which is already interested in two undertakings at Halfslund, is also at the back of the new company.

**THE ELECTRIC SMELTING AND ALUMINUM CO.**, of Cleveland, Ohio, has acquired the business plant and equipment of the COWLES ELECTRIC SMELTING AND ALUMINUM CO., at Lockport, N. Y. The business at Lockport will be continued by the new company under the same management as heretofore (Mr. F. J. Davis, superintendent), but with the advantage of additional capital, better facilities, etc., for conducting the manufacture of the various alloys of aluminium, silicon, manganese, copper, sale of aluminium, etc. In the past both companies had about the same stockholders, but the Electric Smelting and Aluminum Co. held the patents and fought, as well known, to a successful issue, several famous patent litigations, while the Cowles Smelting and Aluminum Co. has been a manufacturing concern at Lockport.

**MAGNESITE.**—In a United States Geological Survey pamphlet, Mr. Charles G. Yale reports on the production of magnesite in 1903. The production in the United States continues to be entirely from California, and during 1903 the quantity reported was 3744 short tons crude, valued at \$10,595, equivalent to 1361 tons calcined, worth \$20,515. The demand for both crude and calcined is limited on the Pacific Coast, and, owing to a freight rate of \$13 to \$15 per ton on shipments to Eastern points, it is not shipped out of California, except to the paper mills in Oregon. The production of California could be quadrupled, if the demands of consumption warranted the increase. The imports of magnesite into the United States in 1903 amounted to 73,534,690 pounds (\$311,396) of calcined, not purified magnesite, and 36,017,637 pounds (\$150,002) of crude magnesite. Most of the imports came from Greece, although some came from Austria. The calcined magnesite, generally in the form of brick, is now universally recognized as the best material for lining basic open hearth furnaces, cement kilns, etc. It may be employed to advantage wherever high temperatures and chemical reactions are usually detrimental to dolomite, chromite, and silica brick. The distinctive characteristics of a magnesite lining are durability, freedom from moisture and silicic acid, and resistance to corrosion when exposed to the action of basic slags and metallic oxides. These qualities make the lining cheaper than most others in the long run. Thus far magnesite bricks have been made in California, though a factory for the purpose is shortly to begin operations at Oakland. The bricks made in this country come from the Fayette Manufacturing Co., of Layton, Pa., and the Harbison-Walker Refractories Co., Pittsburg.

## PERSONAL.

Mr. JOHN S. PECK, of the Westinghouse Electric & Manufacturing Co., has been appointed acting chief electrical engineer of the British Westinghouse Electric & Manufacturing Co. Mr. Peck entered the Westinghouse Co. a little over ten years ago, shortly after graduating from Cornell University. After a short time on the Student Course, he took up engineering work in connection with transformer design and soon became the head of the transformer designing department, which position he has held until the present time. The first signed article, published in the first issue of *ELECTROCHEMICAL INDUSTRY* (September, 1902), was from Mr. Peck's pen and dealt with transformer designs for electrochemical plants. He has contributed a number of valuable papers to the transactions of professional bodies, and taken leading parts in the discussions at their meetings. In this respect also his loss will be much felt.

DR. HANS GOLDSCHMIDT, of Essen-Ruhr, Germany, the distinguished inventor of the aluminothermic process, has sailed for Germany, after having attended the International Electrical Congress. On the eve of his departure a dinner was given to him on October 14, at Delmonico's by Mr. Ernest Stütz, vice-president of the Goldschmidt Thermit Company, who had invited a number of friends of the inventor and his process. The following gentlemen were among them: Mr. R. D. Benson, vice-president, Tidewater Oil Company; Dr. C. F. Chandler, Columbia University; Mr. Hy. Des Angles, superintendent floating equipment, Long Island Railroad; Dr. Charles B. Dudley, chief chemist, Pennsylvania Railroad Company, Altoona, Pa.; Mr. Louis Fischer, United States Commercial Company; Dr. C. Kirchhoff, editor *Iron Age*; Mr. J. Newmark, United States Commercial Company; Mr. Mason D. Pratt, consulting engineer, Harrisburg, Pa.; Mr. W. Boardman Reed, engineer, maintenance and construction, New York City Railway; Dr. J. W. Richards, Lehigh University; Dr. E. F. Roeber, editor *ELECTROCHEMICAL INDUSTRY*, and Mr. Hubert E. Rogers, director, Goldschmidt Thermit Company. Dr. W. H. Wahl, secretary of the Franklin Institute, had sent his regrets to be unable to be present. In opening the series of informal speeches, Mr. Stütz gave an outline of the initial stages of the development of industrial aluminothermics in the United States. Interesting information was given by Dr. Dudley and Mr. des Angles on their results obtained with thermit repairs of broken locomotive frames and steamer shafts, and by Messrs. Pratt and Reed on rail welding. Dr. Goldschmidt spoke in a very suggestive way on the fundamental points of his process and on the developments of aluminothermics abroad, while Dr. Chandler gave some humorous reminiscences of the day when the aluminothermic method was first exhibited at Columbia University.

## DIGEST OF U. S. PATENTS

PRIOR TO JULY, 1902.

Compiled by Byrnes & Townsend,  
Patent Lawyers,

National Union Building, Washington, D. C.

MOLTEN ELECTROLYTES, MISCELLANEOUS.

(Continued from page 434.)

462,567, November 3, 1891, Farnham M. Lyte, London, England.

Produces sodium or potassium carbonate and chlorin. Decomposes sodium nitrate by heating it with calcium carbonate; leaches out the sodium carbonate and converts the nitric oxide fumes into nitric acid by the action of air or oxygen and water; dissolves litharge in the nitric acid; precipitates lead chloride by sodium chloride; and finally fuses and electrolyzes the lead chloride to produce chlorin and lead, which is reoxidized. The electrolytic cell comprises a vessel and bell of enamel iron, or lined with or composed of graphite or earthenware. An anode of graphite depends into the bell, which has a chlorin outlet. A cathode of tinned iron extends through the

bottom of the vessel, which has a tap-hole for the molten lead. 465,369, December 15, 1891, Ludwig Grabau, Hanover, Germany.

A cell for electrolyzing molten salts, especially of sodium, in which the electrodes are separated by a bell or "pole-cell." The bell has hollow walls of refractory material through which water or air is circulated, thereby chilling a protecting and insulating crust of the salt on the walls. The cathode is a depending iron bar, adjustably threaded through the top of the bell, its cross section and resistance being such that the current will heat it and maintain the sodium or other contents of the bell molten. The bell has a lateral outlet at its upper end for the sodium or other cathode product.

469,454, February 23, 1892, Augustus J. Rogers, Milwaukee, Wis.

Closes the tap-hole of a crucible or other vessel for molten electrolytes by cooling and solidifying a plug of the molten electrolyte or deposited metal therein. A carbon resistance tube or rod extends loosely through the tap-hole. When the electric current is cut off from the tube or rod, the molten electrolyte or metal chills in the hole. The lower end of the carbon tube or rod may have a protruding metallic tube to assist in carrying off heat. To open the tap-hole, the tube or rod is heated by electricity until the plug is melted.

473,117, April 19, 1892, Paul Heroult, Neuhausen, Switzerland.

Reduces the resistance of carbon electrodes for use with molten compounds of aluminium, silicon, etc., by placing therein strips or rods of the metal to be recovered, or of an alloying metal. Vertical holes may be bored through the carbon and filled with cast metal; metal plates may be interposed between carbon slabs, or spaced carbon rods may be surrounded by cast metal.

475,498, May 24, 1892, Joseph C. Fraley, Philadelphia, Pa.

To produce iron castings free from strain and lines of crystallization, a helix of wire coated with refractory insulation is embedded in the sand around the mold cavity. Immediately after casting, a rapidly alternating current is passed through the helix and continued until and after the metal solidifies. Cylinders of solid iron or steel may be subjected to similar treatment as the casting, after being heated to a high temperature.

495,600, April 18, 1893, Gustaf O. Rennerfelt, Stockholm, Sweden.

A combined bell and cathode comprising a non-conductive wall and a conductive lining. The bell has a lateral outlet for the deposited metal, to which a suction pump is applied.

502,431, August 1, 1893, Henry H. Eames, Baltimore, Md.

Frees ores from sulphur, phosphorus, or arsenic by heating them in a vertical retort to a temperature below fusion, as cherry red, and passing an electric current through them between carbon-rod electrodes, which depend into the charge. The sulphur is discharged from the ore and falls to the bottom of the vessel, leaving a friable sponge containing the gold and other metals. A current of 15 amperes is specified. Five per cent of carbon may be mixed with the ore. Lime may be added to the charge to remove the sulphur as calcium sulphate.

503,451, August 15, 1893, Willard E. Case, Auburn, New York.

The cell comprises a flat bottom plate of conductive material, e. g., iron, serving as the cathode, and a cylindrical iron casing with a solid lining of salt. The salt may extend between the bottom and casing, to close the joint, or a ring of asbestos may be placed between them. The bottom plate may be protected from the heating flame by a lower layer of fireclay. The anode is a carbon rod depending into the vessel. The salt lining may be cast in a separate mold, may be cast between the iron casing and a temporary core, or may be chilled on the iron casing. The lining may consist of the single salt to be electrolyzed, or of one of the ingredient salts in a mixed electrolyte.



